POLARIZATION PROPAGATOR CALCULATIONS FOR OPEN AND CLOSED SHELL SYSTEMS

BY

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To Shantanu,

With All My Love

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The Polarization Propagator method is employed to calculate excitation energies and transition dipole moments within the Tamm-Dancoff (TDA), Random Phase Approximations (RPA) based on an independent particle state, the generalized Tamm-Dancoff(GTDA) and the Random Phase Approximation(GRPA) based on the Generalized Antisymmetrized Geminal Power wavefunction. The method is also extended to include open shell systems in the GTDA and has been successfully applied to Li atom. Explicit expression for the open shell GRPA is included.

A close examination of the GAGP wavefunction which serves as a 'consistent' reference state to the Polarization Propagator has been carried out. A comparative study of the AGP based RPA and TDA calculations for LiH, Li_2 and He systems

convincingly demonstrates the potential of the AGP to be a consistent reference state.

INTRODUCTION

Observables such as transition energies and transition moments of a molecular system may be evaluated directly by the Polarization Propagator [1]. Spectroscopic properties like nuclear spin-spin coupling constants, dipole and quadrupole moments, radiative lifetimes, Verdet constants, and frequency dependent polarizability are easily understood and calculated within the propagator formalism. Propagators, or the Green's functions as response function to an external field probe, have originally found successful applications in field theory [2], and statistical mechanics [3]. The double time Green's function expressed as a response function referring to directly measurable quantities is particularly appealing for all areas of spectroscopic studies and has been implemented into statistical physics by Zubarev [4] and into quantum chemistry by Linderberg and Ohrn [1]. Calculations of excitation energy by this approach obviate the need for optimizing both ground and excited states. Numerical inaccuracy due to taking the difference of two very large numbers (state energies) to obtain excitation energies is also circumvented by this procedure. The optimized reference state to a polarization propagator must form a basis for a balanced description of both ground and excited states in order to produce accurate excitation energies, and their associated properties. Early quantum chemical calculations of the Polarization Propagator have

applied the linearized time-dependent Hartree Fock (TDHF) [5] or the Random Phase Approximation (RPA), [6], and the Tamm Dancoff Approximation (TDA), [7], using an optimized single determinental (Hartree Fock) reference state [8]. For a complete set of particle-hole $\{a_p^+ a_h\}$ and the hole-particle $\{a_h^+ a_p\}$ operators, a unique set of excitation operators for the RPA has been given by Dalgaard [9],

$$Q_k^+ = \sum_{\mu} \left(Z_{\mu k}\ q_{\mu}^+ \ +\ Y_{\mu k}\ q_{\mu} \right) \tag{1}$$

such that

$$Q_k^+ |\text{Reference state}> = |\text{Excited state, k}> \tag{2}$$

where q_k^+ is a linear combination of particle hole operators, and q_k its adjoint, Z_{rk} and Y_{rk} are the complex expansion coefficients. For a consistent approximation for RPA one must then also fulfill the condition

$$Q_k |\text{Reference state}> = 0 \tag{3}$$

The failure of the Hartree Fock state to satisfy the above condition, has led to several approximations aimed at remedying this inconsistency. A higher RPA which uses multideterminental TDHF by constructing a linear combination

of a HF state and all singlet double excitations out of it has been used, but suffers very often from triplet instabilities [10]. Another attempt to go beyond the simple RPA is the SCPA (self consistent polarization propagator approach) [11]. This approach iterates on the second order density matrix (expressed as

$$\langle a_i^+ a_j a_k^+ a_l \rangle = \lim_{t \to 0} \frac{i}{2\pi} \int_{-\infty}^{\infty} dE\, e^{-iEt} \langle\langle a_i^+ a_j ; a_k^+ a_l \rangle\rangle + \langle a_i^+ a_j \rangle \langle a_k^+ a_l \rangle) \quad [4]$$

until self consistency is achieved. The SCPA and other higher order polarization propagator approaches [12] yield too high values for the excitation energies. Improvements on the SCPA with inclusion of two particle-two hole correction terms are equivalent to second order perturbative schemes of the polarization propagator [13]. While fairly accurate numerical results are achieved with such improved methods, the lack of consistency leads to problems with identification of the excited states of the system, with known spectroscopic states.

It has been established by Linderberg and Ohrn [14], Ohrn and Linderberg [15], using the unitary group parameters as generator coordinates that the consistent reference state for the polarization propagator is necessarily a Generalized

Antisymmetrized Geminal Power (AGP) wavefunction. The GAGP is of same form as the N particle projected Bardeen Cooper Schrieffer (BCS) function used in the theory of superconductivity [16] and nuclear physics [17]. While the GAGP in practice has not proven to be an exact consistent reference to the Polarization Propagator in the RPA the GAGP is a better consistent reference state to the Generalized Tamm Dancoff Approximation (GTDA), than is the single determinantal SCF. The GAGP based GTDA permits us to identify the eigenstates obtained, as spectroscopic excited states. Such an approximation amounts to setting Y = 0 in equation (1), and it has been conjectured that the contribution due to the Y component for GAGP would be smaller than in an uncorrelated reference state as HF To test the validity of such a viewpoint, comparative studies were carried out for He, LiH, and Li_2. These results give a strong indication that indeed, the RPA results are much closer to the TDA when the reference state is an AGP rather than a HF state. These results are tabulated in Chapter Four. These results further indicate that the triplet instability problem is greatly improved by using AGP over HF. The Generalized form of the AGP (GAGP) contains a single determinantal independent particle function that could accommodate core electrons which do not require detailed correlation or accommodate any unpaired electron (for doublet spin systems) which cannot be included in the geminal of the AGP. The use of the generalized form often

proves to be more efficient in comparison with the fully correlated AGF. There is usually no loss in quality of results (by freezing the core orbitals to configurational variation) [18]. The case of the open shell systems is complicated by the fact that even though the adjoints of the excitation operators satisfy the vacuum condition, the GTDA fails to be a consistent approximation for the open shell (spin doublet ground state) GAGF reference state. This has been elucidated in Chapter Three and the problem arises primarily due to the spin degeneracy and the need to span the full spin space. In this case one can only expect to obtain numerical results using the full RPA expression. In a paper by Swanstrøm and Jørgensen [19], the authors have evaluated excitation energies of open shell systems using the perturbative propagator formalism where they have treated the excited state with an unpaired electron as their zeroth order wavefunction and the configuration with an unpaired electron with a β spin as a second order correction to the wavefunction. With the same strategy, one may, in the first approximation, simply consider the configuration of excited states to be consisting of an unpaired electron with α spin only (which is then correct up to first order in the perturbation expansion). It is an interesting excercise to look at the numerical accuracy of this approximation. We have programmed the GTDA for this approximation and used it to evaluate excited states of the Li atom. The first few excitation energies are surprisingly

close to experimental values, but one needs to check such a procedure for larger systems before any conclusions can be drawn. It nonetheless provides an inspiring first step towards developing a generally valid theory, although a more involved numerical procedure is outlined in Chapter Three together with results of these preliminary calculations.

CHAPTER ONE
POLARIZATION PROPAGATOR

Background

We may describe by a double-time Green's function [1] the causal probability amplitude of the density fluctuation function $\rho(t)$, of a pure state, as it responds to a weak external field. The double-time Green's function is expressed as,

$$G(t,t') = \langle\langle \rho(t), \rho(t') \rangle\rangle$$

$$- i\Theta(t-t')\langle 0|\rho^{+}(t)\rho(t')|0\rangle$$

$$- i\Theta(t'-t)\langle 0|\rho^{+}(t')\rho(t)|0\rangle \tag{1-1}$$

where Θ is the Heaviside step function, such that

$$\Theta(t-t') = \begin{cases} 1 & \text{if } t > t' \\ 0 & \text{if } t < t' \end{cases} \tag{1-2}$$

and $|0\rangle$ is the ground state.

Invoking the resolution of the identity in equation (1-1), with a complete set of discrete eigenstates $|m\rangle$, of the hamiltonian H (equation (1-4)), permits us to write, [1],

$$\langle\langle \rho(t); \rho(t') \rangle\rangle = \sum_{m} \Big[i\Theta(t-t')\langle 0|\rho(t)|m\rangle\langle m|\rho(t')|0\rangle$$

$$- i\Theta(t'-t)\langle 0|\rho(t')|m\rangle\langle m|\rho(t)|0\rangle \Big] \tag{1-3}$$

The hamiltonian H is given by

$$H = \sum_{i,j} h_{ij} a_i^{+} a_j + \frac{1}{4} \sum_i \sum_j \sum_k \sum_l \langle ij||kl\rangle a_i^{+} a_j^{+} a_l a_k$$

with

$$h_{ij} = \langle i| \; -\frac{1}{2}\nabla^2 \; + \; \sum_k \frac{Z_k e}{|\overline{R_k - r}|} \; |j\rangle \tag{1-4}$$

Z = the nuclear charge of atom k,

e = electronic charge

R_k = position vector of nucleus k

r = position vector of electron 1

and

$\langle ij||kl\rangle$ = an antisymmetric electron repulsion integral.

The Fourier transformation of the equation (1-3) yields the energy representation of the propagator [1,13],

$$\langle\langle\rho;\rho\rangle\rangle_E = \lim_{\eta \to 0} \sum \left[\frac{\langle 0|\rho|m\rangle\langle m|\rho|0\rangle}{E - \omega_{0m} + i\eta} - \frac{\langle 0|\rho|m\rangle\langle m|\rho|0\rangle}{E - \omega_{0m} - i\eta} \right] \tag{1-5}$$

The small positive number η, has been introduced to produce convergent integrals in the Fourier transformation. The density fluctuation function ρ, may be expanded in a basis set of one particle fermion operators $[\{a_i^{+}a_j\},\ 1 \leq i,j \leq S;$ S= total # of functions in the spin orbital basis $\{u_s\}]$. This permits us to write equation (1-5) in its component form

$$\langle\langle a_i^+ a_j ; a_k^+ a_l \rangle\rangle_E = \lim_{\eta \to 0} \sum_m \left[\frac{\langle 0 | a_i^+ a_j | m \rangle \langle m | a_k^+ a_l | 0 \rangle}{E - \omega_{0m} + i\eta} - \frac{\langle 0 | a_k^+ a_l | m \rangle \langle m | a_i^+ a_j | 0 \rangle}{E - \omega_{0m} - i\eta} \right] \tag{1-6}$$

Equation (1-6) is the Lehman-Källén representation of the propagator. It reveals the salient features of the propagator. Poles occur at the excitation energies of the system with residues, which can be used in, say, the calculation of the dipole transition moments. Thus we see how one may directly calculate spectral properties without formal calculations of excited states.

Procedure For Evaluation Of Propagator

We differentiate equation (1-3) with respect to time and write it in component form as follows, [i]

$$i \frac{\partial}{\partial t} \langle\langle a_i^+ a_j(t), a_k^+ a_l(t) \rangle\rangle = \delta(t-t') \langle | [a_i^+ a_j, a_k^+ a_l] | \rangle + \langle\langle [a_i^+ a_j, H]; a_k^+ a_l \rangle\rangle \tag{1-7}$$

where the time-dependent field operators are expressed in the interaction picture, with use of the time evolution operator, u(t), as

$$a_i^+ a_j(t) = u(t)^+ a_i^+ a_j u(t) \tag{1-8}$$

Equation (1-7) may lead to a hierarchy of Propagators in the following way. The Fourier transform of equation (1-7), yields

$$E\langle\langle a_i^+ a_j ; a_k^+ a_l \rangle\rangle_E = \langle |[a_i^+ a_j , a_k^+ a_l]| \rangle + \langle\langle [a_i^+ a_j , H] ; a_k^+ a_l \rangle\rangle_E \tag{1-9}$$

Decoupling this propagator equation may be conveniently achieved by using the superoperator technique of Goscinski and Lukman [20]. We first introduce a linear space of field operators [9,21,22]

$$h = \{I,\ a_a^+ a_i,\ a_a^+ a_b^+ a_i a_j,\ a_a^+ a_b^+ a_c^+ a_i a_j a_k\ , \ldots\} \tag{1-10}$$

and introduce the superoperator hamiltonian $\hat{H}$, by

$$\hat{H}X = [X, \hat{H}] \tag{1-11}$$

The superoperator identity $\hat{I}$, is defined as

$$\hat{I}X = X \tag{1-12}$$

where X is a general element of vector space V. The superoperator binary product is defined as

$$(x_i|x_j) = \langle|[x_j, x_i^+]_-|\rangle \tag{1-13}$$

Iterating equation (1-9) we obtain,

$$\langle\langle a_i^+a_j; a_k^+a_l\rangle\rangle_E = E^{-1}\langle|[a_i^+a_j, a_k^+a_l]|\rangle + E^{-2}\langle|[[a_i^+a_j, H], a_k^+a_l]|\rangle$$
$$+ E^{-3}\langle|[[[a_i^+a_j, H], H], a_k^+a_l]|\rangle + \ldots \tag{1-14}$$

The application of the superoperator permits us to write equation (1-14) as,

$$\langle\langle a_i^+a_j; a_k^+a_l\rangle\rangle_E = E^{-1}(a_j^+a_i|a_k^+a_l) + E^{-2}(a_j^+a_i|\hat{H}|a_k^+a_l) +$$
$$+ E^{-3}(a_j^+a_i|\hat{H}^2|a_k^+a_l) + \ldots$$
$$= (a_j^+a_i|(E\hat{I} - \hat{H})^{-1}|a_k^+a_l) \tag{1-15}$$

In equation (1-15) we have introduced the superoperator resolvent. In order to bring this expression into matrix form one may use the method of inner projection, introduced to quantum chemistry by Lowdin [23,24] and Lowdin and Lindner [25], and first implemented in the Polarization Propagator approximation [26]. We then express equation (1-15) in its matrix form as,

$$\langle\langle a_i^+ a_j ; a_k^+ a_l \rangle\rangle_E = (a_j^+ a_i | \mathbf{b})(\mathbf{b}|(E\hat{I} - \hat{H})|\mathbf{b})^{-1}(\mathbf{b}|a_k^+ a_l) \qquad (1\text{-}16)$$

The manifold of operators that are particularly simple and interesting for studying excitation processes is the linear single particle operators. We may therefore consider a partitioning of the operator set $|\mathbf{b}|$, into a subset consisting of all possible single particle operators, $\{\mathbf{b}_\nu^+\}$, and the complementary subset, $\{\mathbf{c}_\nu^+\}$, so that

$$\mathbf{b} = \{\mathbf{b}_\nu^+, \mathbf{c}_\nu^+\} ; \qquad (1\text{-}17)$$

With this partitioning the top left-hand block of the propagator may be written as the following [27],

$$\begin{aligned}\langle\langle a_i^+ a_j ; a_k^+ a_l \rangle\rangle_E = {} & (a_j^+ a_l | \mathbf{b}_\nu^+)(z\mathbf{I}_\nu - \mathbf{H}_\nu - \mathbf{\Sigma}^-(z))^{-1}(\mathbf{b}_\nu^+ | a_k^+ a_l) \\ & - (a_l^+ a_k | \mathbf{b}_\nu^+)(\bar{z}\mathbf{I}_\nu - \mathbf{H}_\nu - \mathbf{\Sigma}^+(z))^{-1}(\mathbf{b}_\nu^+ | a_i^+ a_j) \\ & + \delta \end{aligned} \qquad (1\text{-}18)$$

In the above expression,

$$\mathbf{I}_\nu = (\mathbf{b}_\nu^+ | \mathbf{b}_\nu^+)$$

$$\mathbf{H}_\nu = (\mathbf{b}_\nu^+ | \hat{H} | \mathbf{b}_\nu^+)$$

$\bar{z}$ is the complex conjugate of z.

$$\mathbf{\Sigma}^{\pm}(z) = (\mathbf{b}_\nu^+ | \hat{H} | \mathbf{c}_\nu^+)(\mathbf{c}_n^+ | (z\hat{I} \pm \hat{H} | \mathbf{c}_\nu^+)(\mathbf{c}_\nu^+ | \hat{H} | \mathbf{b}_\nu^+)$$

and

$$\delta = \langle a_i^+ a_j \rangle \langle a_k^+ a_l \rangle \frac{2i \text{ Im } z}{| z |^2} \qquad (1\text{-}19)$$

Equation (1-18) represents the exact propagator. All possible approximations that will be considered originate from this equation. In the following section, the polarization propagator corresponding to the one particle excitation operator will be outlined. The next section deals with operators that generate singlet and triplet states out of closed shell(S - 0) system. Since the creation of a complete space of doublet excited states out of a doublet ground state requires a particular type of two particle operators, the open shell propagator will be discussed separately in chapter three

Polarization Propagator Expression

Introducing a set of excitation operators $\{q^+,q\}$ which create states with correct spin symmetry when acting on a singlet state (such as singlets, triplets etc.), we may write,

$$q_{ij}^+ = c_j(a_i^+ a_j \pm a_{\bar{i}}^+ a_{\bar{j}}) \mp c_i(a_j^+ a_i \pm a_{\bar{j}}^+ a_{\bar{i}})$$

$$q_{ij} = c_j(a_j^+ a_i \pm a_{\bar{j}}^+ a_{\bar{i}}) \mp c_i(a_i^+ a_j \pm a_{\bar{i}}^+ a_{\bar{j}}) \qquad (1\text{-}20)$$

where the occupation number n_j of spin orbital j in the reference state is greater than the occupation number n_i of

spin orbital i, and c_i, c_j are coefficients for the excitation operators. The upper signs corresponds to an excitation operator for a spin singlet state and the lower signs to an operator for a triplet state. The most general one particle excitation operator may then be constructed by a linear superposition of the q^+ 's, and the q 's [9]. The new set of excitation operators $\{Q_\nu^+, Q_\nu\}$ may be written as,

$$\begin{bmatrix} Q^+ & Q \end{bmatrix} = \begin{bmatrix} q^+ & q \end{bmatrix} \begin{bmatrix} Z & \bar{Y} \\ Y & \bar{Z} \end{bmatrix} \tag{1-21}$$

with $\{Z,Y\}$ as expansion coefficients for general excitation operators.

For $\{ Q^+, Q \}$ to form a set of excitation operators, Dalgaard [9] proved the following theorem. Let $|0\rangle$ and $|\lambda\rangle$ be arbitrary N-electron states, which satisfy $\langle 0|\phi_0\rangle \neq 0$ and $\langle 0|\lambda\rangle = 0$. If the matrix $\langle [q,q^+]\rangle$ is non singular, there is one and only one, "excitation operator" of the form,

$$Q_\lambda^+ = \sum_\mu \left(q_\mu^+ Z_{\mu\lambda} + q_\mu Y_{\mu\lambda} \right) \tag{1-22}$$

such that,

$$\begin{aligned} |\lambda\rangle &= Q_\lambda^+|0\rangle \\ Q_\lambda|0\rangle &= 0 \end{aligned} \tag{1-23}$$

In the above theorem $|\phi_0\rangle$ is an N-electron state in the Fock space and can be written as

$$|\phi_0\rangle = \prod_{i=1}^{N} a_i^+ \; |vac\rangle \tag{1-24}$$

The polarization propagator P(E) is formally expressed as

$$P(E) = \begin{bmatrix} \langle\langle q ; q^+ \rangle\rangle & \langle\langle q ; q \rangle\rangle \\ \langle\langle q^+ ; q^+ \rangle\rangle & \langle\langle q^+ ; q \rangle\rangle \end{bmatrix} \tag{1-25}$$

Incorporation of the propagator expression of equation (1-18) into equation (1-25) yields the following matrix equation,

$$P(E) = \begin{bmatrix} \lambda & 0 \\ 0 & -\lambda \end{bmatrix} \begin{bmatrix} E\lambda - A & B \\ B^* & -(E\lambda + A^*) \end{bmatrix}^{-1} \begin{bmatrix} \lambda & 0 \\ 0 & -\lambda \end{bmatrix} \tag{1-26}$$

With the notation,

$$A = \langle |[q,[H,q^+]]|\rangle$$

$$B = \langle |[q,[H,q]]|\rangle \tag{1-27}$$

and the set $\{q^+,q\}$ satisfy the relations,

$$\langle|[q\ ,\ q^{+}]|\rangle = \lambda = -\langle|[q^{+},\ q]|\rangle$$
$$\langle|[q^{+},\ q^{+}]|\rangle = 0 = \langle|[q\ ,\ q]|\rangle \tag{1-28}$$

Diagonalization of propagator matrix is accomplished by a series of transformations [14,28], so one may express the propagator as,

$$P(E) = \begin{bmatrix} \lambda^{1/2} & 0 \\ 0 & \lambda^{1/2} \end{bmatrix} \begin{bmatrix} Z & Y \\ Y & Z \end{bmatrix} \begin{bmatrix} (EI - \omega)^{-1} & 0 \\ 0 & -(EI + \omega)^{-1} \end{bmatrix} \begin{bmatrix} Z^{+} & Y^{+} \\ Y^{+} & Z^{+} \end{bmatrix} \begin{bmatrix} \lambda^{1/2} & 0 \\ 0 & \lambda^{1/2} \end{bmatrix} \tag{1-29}$$

The eigenvalues ω, of the propagator are solutions of the eigenvalue equation,

$$\begin{bmatrix} A & B \\ B^{*} & A^{*} \end{bmatrix} \begin{bmatrix} Z \\ Y \end{bmatrix} = \omega \begin{bmatrix} \lambda & 0 \\ 0 & -\lambda \end{bmatrix} \begin{bmatrix} Z \\ Y \end{bmatrix} \tag{1-30}$$

Even though the propagator matrix on the left hand side of equation (1-30) is itself hermitian and has real eigenvalues [25], this generalized eigenvalue equation may have complex eigenvalues. This is related to the stability of the optimized reference state with respect to symmetry breaking, which will be discussed in Chapter Two. If the reference state is stationary with respect to the variational parameters then the propagator matrix is in fact the Hessian [30] of the variational problem (see Chapter Two).

Random Phase Approximation

When the polarization propagator calculations are based on the single determinant, one has the RPA which was originally used in nuclear physics [6]. Comparison of the components of the propagator equation (1-18) with the Lehmann-Källén representation permits me to identify the following relationships, [14,31]

$$\lambda_k^{1/2} z_{km} = \langle 0|q_k|m\rangle \; ; \qquad \lambda_k^{1/2} Y_{km} = \langle m|q_k|0\rangle \; ;$$
$$\lambda_1^{1/2} z_{1m}^* = \langle m|q_1^+|0\rangle \; ; \qquad \lambda_1^{1/2} Y_{1m}^* = \langle 0|q_1^+|m\rangle \tag{1-31}$$

And since in the process of diagonalization of the propagator we require the condition,

$$Z^+Z - Y^+Y = 1 \tag{1-32}$$

We obtain the condition that,

$$\langle m|\sum_k \lambda_k^{-1/2}(q_k^+ z_{km} - q_k Y_{km}^*|0\rangle = 1 \tag{1-33}$$

which leads us to the expression for the excitation operators (Q_m^+).

$$\sum_k \lambda_k^{-1/2}(q_k^+ z_{km} - q_k Y_{km}^*) = Q_m^+ \tag{1-34}$$

Ideally we require the operators $\{Q^+\}$ to be such that their adjoints $\{Q\}$ annihilate the reference state,

$$Q_m|0\rangle = 0 , \qquad \text{for all } m \qquad (1\text{-}35)$$

It is however well known that the Hartree Fock reference state does not satisfy this vacuum condition (1-35) and is thus not a consistent reference state to the RPA [10,14,15]. In other words,

$$Q_m|HF\rangle \neq 0 \qquad \text{for all } m \qquad (1\text{-}36)$$

only if $Y = 0$ in equation (1-34). One may set $Y=0$ as an approximation to the RPA, known in the literature as the Tamm Dancoff approximation (TDA).

Tamm Dancoff Approximation

The inconsistency of the RPA is rooted in the interaction of the reference state with excited states through the hamiltonian (which is symbolized by the B matrix in the propagator). Consistency requires that the B matrix be zero identically. In the absence of any reference function which fulfils this requirement exactly, one may as an approximation set the B blocks to zero and obtain the Tamm Dancoff Approximation as a consistent approximation to the RPA. Setting the B block to zero, the Y vector is

eliminated and the excitation operators for HF, $\{Q_k^+\}$, are then simple particle-hole operators,

$$Q_k^+ = a_i^+ a_j \pm a_{\bar{i}}^+ a_{\bar{j}} \qquad 1 \leq j \leq N;\ N < i \leq S \tag{1-37}$$

Where N is the total number of doubly occupied orbitals and 2S is the total number of basis functions. It is obvious that the Q_k(TDA) satisfy the vacuum condition since the i orbitals are unoccupied in the ground state and hence annihilate the reference state.

With this background, we will now look into a more general and correlated wavefunction which may be a suitable reference function for the polarization propagator. As mentioned in the introduction, the Generalized Antisymmetrized Geminal Power wavefunction(GAGP) is such a reference state [14,15]. While in the past few years the AGP-TDA ansatz has produced some interesting results [32], in this project we have developed and investigated several aspects of the AGP. We have developed the generalized version of the GTDA and GRPA based on the GAGP and also made comparative studies of the GTDA and GRPA to estimate the measure of consistency of this ansatz. Our calculations with the AGP ansatz are compared with those based on the HF reference state. The next chapter contains a discussion of the GAGP wavefunction.

CHAPTER TWO
THE REFERENCE STATE

Generalized Antisymmetrized Geminal Power Wavefunction

The AGP function, formulated as an N-particle projected BCS (Bardeen, Cooper, Schrieffer) function and alternatively known as the Schafroth-condensed pair wavefunction [17], has been applied successfully in the theory of superconductivity. Efforts directed towards obtaining a proper reference state for the polarization propagator have led to suggestions by Linderberg and Ohrn [14], and Ohrn and Linderberg [15] for employing AGP as the reference state for polarization propagator. A generalized AGP function was also established by Goscinski and Weiner [33] to be the correct reference state for the self consistent one particle-hole propagator (SCIPHP). Furthermore, because of its sparse and well structured first and second order density matrices, the AGP function has been explored by Coleman [34], Nakamura [35], and others in connection with the N-representability problem. Certain early attempts with the AGP reference state had been rather discouraging because of inefficient computational schemes. However, in recent times sophisticated optimizing strategy built on exploiting the particularly well-structured characteristics of first and second order density matrices of the AGP has proved the wavefunction gives an efficient description of electron correlation

Functional Form

The basic information in an AGP wavefunction is contained in a single geminal G(ij), which represents a pair of electrons i,j. The geminal may be expressed as a superposition of all two electron determinants $|\phi_k\phi_{\bar{k}}|$, weighted by factors g_k. We may express G^+, creating a geminal on the vacuum as,

$$G^+(ij) = \sum_{1 \le k \le a} g_k \left\{ (a_k^+(i)a_{\bar{k}}^+(j) \; - \; a_{\bar{k}}^+(i)a_k^+(j) \right\} \qquad (2\text{-}1)$$

where 2a is the total number of functions in the basis set. ϕ_k and $\phi_{\bar{k}}$ are natural spinorbitals (nso's) that contain the same spatial function but with α and β spins respectively.

Thus for a system with N(even) electrons, an AGP function is an antisymmetrized N/2 power of the geminals [14,15],

$$AGP = (C_{N/2})^{-1}\{G^+\}^{N/2}\ |vac\rangle \qquad (2\text{-}2)$$

where G(i,j) may also be written in the natural spinorbital basis as

$$G(i,j) = \sum_k g_k \left[\phi_k(i)\phi_{\bar{k}}(j) - \phi_{\bar{k}}(i)\phi_k(j) \right] \qquad (2\text{-}3)$$

$C_{N/2}$ is the normalization constant and consists of a symmetric function S of order N/2, having the following form

$$C_{N/2} = \sum_{1 \leq i_1 < i_2 \ldots i_k \leq s} \nu_{i_1} \nu_{i_2} \ldots \nu_{i_k} \tag{2-4}$$

$$= S_{N/2}$$

where,

$$\nu_i = g_i^* g_i = |g_i|^2 \tag{2-5}$$

The symmetric functions are defined such that [34],

$$S_N = \begin{cases} 0 & \text{if } N < 0, \text{ or } N > s \\ \Sigma\, \nu_{i_1} \nu_{i_2} \ldots \nu_{i_N} & 1 \leq i_1 < \ldots i_N \leq s \\ 1 & \text{if } N = 0 \end{cases} \tag{2-6}$$

The natural spinorbitals of the geminal are also the natural spinorbitals of the AGP function. Even though the AGP expression in equation (2-2) is restricted to spin singlet by doubly occupying each spatial orbital k in the geminal, a general expansion may consist of pairings that have both singlet and triplet combinations. This results in an AGP from which one may project out a certain spin for a pure spin state. Such an expansion has already been considered [36], but the construction did not appear to be very useful and is rather cumbersome. Sangfelt and Goscinski [37] have

also considered two different geminals in the AGP with interesting results for the ground state of Be. In this case the total energy of the system is the same as the MCSCF total energy with the same basis. But it is important to note that a true AGP function is a power function of a single geminal It is often convenient to attach to the AGP function, an independent particle factor (IPF) Φ, that can account for molecular orbitals which are essentially uncorrelated, such as the core and some inner shell electrons in a reasonably large system. The IPF component also becomes essential for calculations involving open shell systems (with odd number of electrons) to accomodate the unpaired electrons. The Generalized Antisymmetrized Geminal Power (GAGP) wavefunction for N electrons is formulated as an antisymmetrized product of AGP and IPF components, containing k geminals and N-2k IPF functions.

$$\mathrm{GAGP} = \{C \sqrt{(N-2k)!}\}^{-1}\, O_{AS} \left\{ G^{+} \right\}^{k} a^{+}_{2k+1} \cdots a^{+}_{N} |\mathrm{vac}\rangle \tag{2-7}$$

The AGP wavefunction contains a very large number of configurations, $\binom{n}{k}$ with much smaller number (n) of the variational parameters g. The energy fuctional E(C,g), which is a function of a set of orbital coefficients C, and a set of geminal expansion coefficients g, is represented by

$$E(C,g) = \frac{\langle GAGP | H | GAGP \rangle}{\langle GAGP | GAGP \rangle} \qquad (2\text{-}8)$$

Since the hamiltonian consists of at most two-particle interaction terms, one can express the above energy expression, by means of a reduced hamiltonian K_H, and second order density matrix $D^{(2)}$ [38], in the following form,

$$E = \mathrm{Tr}[\, K_H \, D^{(2)}(\Psi_{gagp})] \qquad (2\text{-}9)$$

$D^{(2)}(g)$ is the second order density matrix of the GAGP. Equation (2-9) is much more attractive than equation (2-8) computationally because of reduced dimension, however (2-9) cannot be used unless the second order density matrix corresponds to states in N-dimensional Hilbert space. This is known in the literature as the N-representability problem [39]. For the GAGP function, the 2-matrix is N-representable and we can use equation (2-9) to compute the energy quite simply. We use second quantized operators to describe the reduced hamiltonian and 2-density as follows.

The reduced hamiltonian K_H has the form,

$$\begin{aligned} K_H = \sum_{1 \le i < j \le 2m} \Big\{ & \binom{N}{2}^{-1} H_0 (\delta_{jl}\delta_{ik} - \delta_{jk}\delta_{il}) \\ & + (N-1)^{-1} (H_{ik}\delta_{jl} + H_{jl}\delta_{ik} - H_{il}\delta_{jk} - H_{jk}\delta_{il}) \\ & + \langle ij || kl \rangle \Big\} \, a_i^{+} a_j^{+} a_l a_k \end{aligned} \qquad (2\text{-}10)$$

The only possible types of non-zero second order density matrix elements (34) are summarized below :

$$D_a^{(2)} = \langle GAGP|a_i^{+}a_{\bar{i}}^{+}a_{\bar{j}}a_j|GAGP\rangle = g_i^{*}g_j \frac{S_{N-1}^{(i,j)}}{S_N}$$

$$= g_i^{*}g_j \frac{\partial^2 S_{N+1}}{\partial n_i \partial n_j} / S_N \qquad (2\text{-}11)$$

is a square matrix of order $\binom{k}{2} + k$

$$D_b^{(2)} = \left.\begin{matrix} \langle GAGP|a_j^{+}a_i^{+}a_i a_j|GAGP\rangle \\ \langle GAGP|a_{\bar{j}}^{+}a_{\bar{i}}^{+}a_{\bar{i}}a_{\bar{j}}|GAGP\rangle \\ \langle GAGP|a_j^{+}a_i^{+}a_{\bar{i}}a_j|GAGP\rangle \\ \langle GAGP|a_{\bar{j}}^{+}a_i^{+}a_i a_{\bar{j}}|GAGP\rangle \end{matrix}\right\} = n_i^{*}n_j \frac{S_{N-2}^{(i,j)}}{S_N} = n_i^{*}n_j \frac{\partial^2 S_N}{\partial n_i \partial n_j} / S_N \qquad (2\text{-}12)$$

is a diagonal matrix of order $\binom{k}{2}$

$$D_c^{(2)} = \left.\begin{matrix} \langle GAGP|a_j^{+}a_b^{+}a_b a_j|GAGP\rangle \\ \langle GAGP|a_{\bar{j}}^{+}a_{\bar{b}}^{+}a_{\bar{b}}a_{\bar{j}}|GAGP\rangle \\ \langle GAGP|a_j^{+}a_{\bar{b}}^{+}a_{\bar{b}}a_j|GAGP\rangle \\ \langle GAGP|a_{\bar{j}}^{+}a_b^{+}a_b a_{\bar{j}}|GAGP\rangle \end{matrix}\right\} = |g_j|^2 \frac{S_{N-1}^{(j)}}{S_N} = |g_j|^2 \frac{\partial S_N}{\partial n_j} / S_N \qquad (2\text{-}13)$$

is a k*(N-2k) order diagonal matrix

$$D_d^{(2)} = \left.\begin{matrix} \langle GAGP|a_c^{+}a_b^{+}a_b a_c|GAGP\rangle \\ \langle GAGP|a_{\bar{c}}^{+}a_{\bar{b}}^{+}a_{\bar{b}}a_{\bar{c}}|GAGP\rangle \\ \langle GAGP|a_c^{+}a_{\bar{b}}^{+}a_{\bar{b}}a_c|GAGP\rangle \\ \langle GAGP|a_{\bar{c}}^{+}a_b^{+}a_b a_{\bar{c}}|GAGP\rangle \end{matrix}\right\} = \quad 1 \tag{2-14}$$

is a unit matrix of order 2N-k

In the above equations (2-11 through 2-14), spin orbitals are ordered such that $1 \leq i,j \leq k$, $k+1 \leq b,c \leq (N-2k)$. Superscripts on the symmetric functions indicate exclusion of the geminal coefficients corresponding to those orbitals in the symmetric functions. It is to be noted that there are (N-2k) elements of the $D_c^{(2)}$ block that are identical to each diagonal element of the $D_a^{(2)}$ block. For the calculation of energy, only the trace of $K_H D^{(2)}$ is necessary and since the second order density matrix is block diagonalized, one only requires the corresponding diagonal blocks of the reduced hamiltonian K_H, which we may denote by K_a, K_b, K_c, and K_d. Each block of K run through the same indices as the two density. The energy expression is quite simply written as,

$$\begin{aligned} E(C, g) &= (K_a + K_c)\, D_a^{(2)} + K_b\, D_b^{(2)} + K_d \cdot 1 \\ &= \sum_{pq} \Big[\big((K_a)_{pq} + (N-2k)(K_c)_{pq}\delta_{pq} \big) (D_a^{(2)})_{pq} \\ &\quad + \sum_q (K_b)_{qq} (D_b^{(2)})_{qq} + \sum_q (K_d)_{qq} \Big] \end{aligned} \tag{2-15}$$

The AGP wavefunction is optimized with respect to both

orbital and geminal expansion coefficients, and in the case of GAGP, the IPF orbitals are also allowed to relax. Details of optimization of (G)AGP wavefunction have been developed by Weiner and Goscinski (40), Ortiz, Weiner and Ohrn (41). A two-step procedure is followed for optimizing the GAGP function, with no coupling between orbital and geminal optimizations. A minimum point on the energy surface is obtained by requiring that the first derivative (gradient) with respect to orbital and geminal coefficients be zero and the second derivative (hessian) be positive. Explicit expressions for obtaining orbital gradient and hessian are presented in the next section. All the necessary expressions for geminal coefficient variation were derived by Jensen, Weiner and Ohrn (42) and are identical for both AGP and GAGP functions.

Orbital Optimization

The variation of the energy functional with respect to orbital and geminal coefficients is given by,

$$E(\lambda,g) =$$

$$\mathrm{Tr}\Big(\exp\Big[-i\sum_{r>s} \mathrm{Re}\ \lambda_{rs}(a_r^+a_s - a_s^+a_r) + i\mathrm{Im}\ \lambda_{rs}(a_r^+a_s + a_s^+a_r)\Big].$$

$$K_H \exp\Big(i\sum_{p>q} \mathrm{Re}\ \lambda_{pq}(a_p^+a_q - a_q^+a_p) - i\mathrm{Im}\ \lambda_{pq}(a_p^+a_q + a_q^+a_p)\Big)D^{(2)}(g)\Big) \tag{2-16}$$

where $\{\lambda_{rs}\}$ is a set of complex numbers that parametrise the unitary transformation. If the energy function is expanded around $\lambda \to 0$, in a Taylor series and the expansion series is truncated through second order, then we can write the following equation,

$$E(\lambda,g) = E(0,g) + \lambda.\nabla_{\lambda} E(0,g) + \frac{1}{2} \lambda^{t} \nabla_{\lambda}^{2} E(0,g) \lambda \qquad (2\text{-}17)$$

At a stationary point, the gradient is zero, $\nabla_{\lambda} E(\lambda,g) = 0$. This allows us to obtain an expression for λ_{min} from the first derivative of equation (2-17), with respect to λ. At minimum point we also require that the hessian must be positive, ie $\nabla^{2} E(\lambda,g) > 0$. We thus obtain the relationship,

$$\lambda_{min}^{t} = - \frac{\nabla_{\lambda} E(0,g)}{\nabla_{\lambda}^{2} E(0,g)} \qquad (2\text{-}18)$$

The direction and length of the rotation of the spin orbitals is given by λ_{min}^{t}, which then generates the new set of transformed orbitals, and the process is repeated until the norm of the gradient is of desired smallness. The gradient and hessian terms can be quite complicated, if the Taylor's expansion is performed around points other than $\lambda = 0$. To avoid such complication the reduced Hamiltonian is transformed to the current NSO basis on each iteration. In

our calculation we have restricted to real singlet variations only. The gradient with respect to element Re λ_{kl} is

$$\nabla_{kl}(\lambda_{min},g) = \mathrm{Tr}\left(\{[e_k^+e_l - e_l^+e_k],\ K_H]D^{(2)}\right) \qquad (2\text{-}19)$$

When the commutator in (2-19) is expanded, we obtain by rearrangement, [40]

$$\nabla_{kl}(\lambda_{min},g) = \mathrm{Re}\ \ \mathrm{Tr}\{\ (e_k^+e_l)[K_H,D^{(2)}]\} \qquad (2\text{-}20)$$

which can be rewritten as

$$\nabla_{kl}(\lambda_{min},g) = \mathrm{Re}\ \ \mathrm{Tr}\{\ \sum_r |\phi_k\phi_r\rangle\langle\phi_r\phi_l|[K_H,D^{(2)}]\} \qquad (2\text{-}21)$$

ϕ_k referring to spin orbital k of the GAGF, and so on.

or,

$$\nabla_{kl}(\lambda_{min},g) = \mathrm{Re}\ \ \mathrm{Tr}\{\ \sum_r \langle\phi_k\phi_r|[K_H,D^{(2)}]|\phi_r\phi_l\rangle\} \qquad (2\text{-}22)$$

or,

$$\nabla_{kl}(\lambda_{min},g) = \mathrm{Re}\ \left(\ \sum_r [K_H,D^{(2)}]_{krlr}\right)$$

$$= \mathrm{Re} \sum_{r,s,t}\left[(K_H)_{krst}\ D^{(2)}_{stlr} - D^{(2)}_{krst}(K_H)_{stlr}\right]$$

$$(2\text{-}23)$$

As the optimization is restricted to singlet variation, spin orbitals k and l are either both of α spins or of β spins, while the summation goes over all possible combinations of

spins. Explicit formulas for the gradient are included in appendix 1.

We now proceed to the evaluation of the orbital hessian. We may expand the right hand side of equation (2-16) in powers of real and imaginary parts of λ, leading to the following form:

$$E(\lambda, g) =$$

$$\mathrm{Tr}\Big(\Big\{1 - i\sum_{p>q}\Big(\mathrm{Re}\,\lambda_{pq}(a_p^+a_q - a_q^+a_p) + i\mathrm{Im}\,\lambda_{pq}(a_p^+a_q + a_q^+a_p)\Big) -$$

$$-\frac{1}{2}\Big[\sum_{p>q}\Big(\mathrm{Re}\,\lambda_{pq}(a_p^+a_q - a_q^+a_p) + i\mathrm{Im}\,\lambda_{pq}(a_p^+a_q + a_q^+a_p)\Big)\Big]^2 + ..\Big)$$

$$K_H\Big\{1 + i\sum_{r>s}\Big(\mathrm{Re}\,\lambda_{rs}(a_r^+a_s - a_s^+a_r) + i\mathrm{Im}\,\lambda_{rs}(a_r^+a_s + a_s^+a_r)\Big) -$$

$$-\frac{1}{2}\Big[\sum_{r>s}\Big(\mathrm{Re}\,\lambda_{rs}(a_r^+a_s - a_s^+a_r) + i\mathrm{Im}\,\lambda_{rs}(a_r^+a_s + a_s^+a_r)\Big)\Big]^2 + ..\Big\}D^{(2)}\Big) \qquad (2\text{-}24)$$

The infinitesimal generators of the unitary transform U can be symmetry adapted leading to a symmetry blocking of the hessian. We work out an example with the singlet transformation operator $[X_{pq}^+]_s$ (replacing the simple field operators in equation (2-24)) defined as,

$$X_{pq,s}^+ = a_p^+a_q + a_{\bar{p}}^+a_{\bar{q}}$$

$$X_{pq,s} = a_q^+a_p + a_{\bar{q}}^+a_{\bar{p}} \qquad (2\text{-}25)$$

so that the unitary transformation of the energy functional may written as,

$$E(\lambda,g) =$$
$$\mathrm{Tr}\Big[\Big\{1 - i\sum_{p>q}\Big(\mathrm{Re}\ \lambda_{pq}(X^{+}_{pq} - X_{pq}) + i\mathrm{Im}\ \lambda_{pq}(X^{+}_{pq} + X_{pq})\Big) -$$
$$-\frac{1}{2}\Big[\sum_{p>q}\Big(\mathrm{Re}\ \lambda_{pq}(X^{+}_{pq} - X_{pq}) + i\mathrm{Im}\ \lambda_{pq}(X^{+}_{pq} + X_{pq})\Big)\Big]^2 + ..\Big)$$
$$X_H\ \Big\{1 + i\sum_{r>e}\Big(\mathrm{Re}\ \lambda_{re}(X^{+}_{re} - X_{re}) + i\mathrm{Im}\ \lambda_{re}(X^{+}_{re} + X_{re})\Big) -$$
$$-\frac{1}{2}\Big[\sum_{r>e}\Big(\mathrm{Re}\ \lambda_{re}(X^{+}_{re} - X_{re}) + i\mathrm{Im}\ \lambda_{re}(X^{+}_{re} + X_{re})\Big)\Big]^2 + ..\Big)D^{(2)} \tag{2-26}$$

The ijkl'th element of the hessian may be constructed by taking the second derivative of the energy functional with respect to parameters λ_{ij} and λ_{kl}. Since the set $\{\lambda\}$ is a parameter set and the trace operator is linear, equation (2-26) can be written as a sum of traces, with appropriate factors of products of λ's outside the trace operation. Taking the second derivatives and evaluating the hessian elements around λ=0, leads to immense simplification of the expression as illustrated in the following steps. The singlet variation may split up into four components depending on the variational parameter being real, imaginary or complex. We will discuss these four blocks of the singlet hessian separately.

1)Variation with respect to Re λ_{ij} and Re λ_{kl} gives,

$$\nabla^2 E(\lambda,g)_{ijkl}\big|_{\lambda\to 0} =$$
$$\mathrm{Tr}\Big[\Big\{(X^{+}_{ij} - X_{ij})X_H(X^{+}_{kl} - X_{kl}) + (X^{+}_{kl} - X_{kl})X_H(X^{+}_{ij} - X_{ij})$$
$$-\frac{1}{2}\ \Big[(X^{+}_{ij} - X_{ij})(X^{+}_{kl} - X_{kl})X_H + (X^{+}_{ij} - X_{ij})(X^{+}_{kl} - X_{kl})X_H$$
$$+ X_H(X^{+}_{ij} - X_{ji})(X^{+}_{kl} - X_{lk}) + X_H(X^{+}_{kl} - X_{kl})(X^{+}_{ij} - X_{ij})\Big]\Big\}D^{(2)}\Big] \tag{2-27}$$

Introducing the following notation,

$$A_{ijkl} = Tr\left[\left(\left[X^{+}_{ij}, \left[X_H, X^{+}_{kl}\right]\right] + \left[X^{+}_{kl}, \left[X_H, X^{+}_{ij}\right]\right]\right)D^{(2)}\right]$$

$$B_{ijkl} = Tr\left[\left(\left[X^{+}_{ij}, \left[X_H, X_{kl}\right]\right] + \left[X^{+}_{kl}, \left[X_H, X_{ij}\right]\right]\right)D^{(2)}\right] \qquad (2-28)$$

Equation (2-27) may be written in symbolic form as

$$\nabla^2 E(\lambda, g)_{ijkl}\Big|_{\lambda\to 0} = \frac{1}{2}\left(A_{ijkl} - B_{ijkl} - B^{+}_{ijkl} + A^{+}_{ijkl}\right)$$
$$= Re(A - B)_{ijkl} \qquad (2-29)$$

In equation (2-28) we have used the fact that the expectation value of the adjoint of an operator is the complex conjugate of the expectation value of the operator.

2)Variation with respect to Im λ_{ij} and Im λ_{kl} gives,

$$\nabla^2 E(\lambda, g)_{ijkl}\Big|_{\lambda\to 0} =$$
$$Tr\Big[-\Big\{(X^{+}_{ij} + X_{ij})X_H(X^{+}_{kl} + X_{kl}) + (X^{+}_{kl} + X_{kl})X_H(X^{+}_{ij} + X_{ij})$$
$$-\frac{1}{2}\Big[(X^{+}_{ij} + X_{ij})(X^{+}_{kl} + X_{kl})X_H + (X^{+}_{ij} + X_{ij})(X^{+}_{kl} + X_{kl})X_H$$
$$+ X_H(X^{+}_{ij} + X_{ij})(X^{+}_{kl} + X_{1k}) + X_H(X^{+}_{kl} + X_{kl})(X^{+}_{ij} + X_{ij})\Big]\Big\}D^{(2)}\Big] \qquad (2-30)$$

Equation (2-29) can thus be written symbolically as

$$\nabla^2 E(\lambda,g)_{ijkl}\Big|_{\lambda\to 0} = -\frac{1}{2}\left(A_{ijkl} + B_{ijkl} + B^{+}_{ijkl} + A^{+}_{ijkl}\right)$$
$$= -\,\mathrm{Re}(A + B)_{ijkl} \tag{2-31}$$

3) Variations with respect to Re λ_{ij} and Im λ_{kl} yields the follwing expression

$$\nabla^2 E(\lambda,g)_{ijkl}\Big|_{\lambda\to 0} =$$
$$\mathrm{Tr}\Big[i\Big\{(x^{+}_{ij} - x_{ij})\kappa_B(x^{+}_{kl} + x_{kl}) + (x^{+}_{kl} + x_{kl})\kappa_H(x^{+}_{ij} - x_{ij})$$
$$-\frac{1}{2}\big\{(x^{+}_{ij} - x_{ij})(x^{+}_{kl} + x_{kl})\kappa_H + (x^{+}_{ij} - x_{ij})(x^{+}_{kl} + x_{kl})\kappa_B$$
$$+ \kappa_H(x^{+}_{ij} - x_{ij})(x^{+}_{kl} + x_{lk}) + \kappa_H(x^{+}_{kl} + x_{kl})(x^{+}_{ij} - x_{ij})\big\}\Big\}D^{(2)}\Big] \tag{2-32}$$

Which has the following symbolic represention

$$\nabla^2 E(\lambda,g)_{ijkl}\Big|_{\lambda\to 0} = \frac{1}{2}\left(A_{ijkl} - B_{ijkl} + B^{+}_{ijkl} - A^{+}_{ijkl}\right)$$
$$= -\,\mathrm{Im}(A + B)_{ijkl} \tag{2-33}$$

4) We obtain the hessian with respect to Im λ_{ij} and Re λ_{kl} to be

$$\nabla^2 E(\lambda,g)_{ijkl}\Big|_{\lambda\to 0} =$$
$$\mathrm{Tr}\Big[i\Big\{(x^{+}_{ij} + x_{ij})x_B(x^{+}_{kl} - x_{kl}) + (x^{+}_{kl} - x_{kl})\kappa_H(x^{+}_{ij} - x_{ij})$$
$$-\frac{1}{2}\big\{(x^{+}_{ij} + x_{ij})(x^{+}_{kl} + x_{kl})x_H + (x^{+}_{ij} + x_{ij})(x^{+}_{kl} - x_{kl})x_H$$
$$+ \kappa_B(x^{+}_{ij} + x_{ji})(x^{+}_{kl} - x_{lk}) + \kappa_H(x^{+}_{kl} - x_{kl})(x^{+}_{ij} + x_{ij})\big\}\Big\}D^{(2)}\Big] \tag{2-34}$$

which may rewritten in symbolic form as

$$\nabla^2 E(\lambda,g)_{ijkl}\Big|_{\lambda\to 0} = \frac{1}{2}\left\{A_{ijkl} - B_{ijkl} + B^{+}_{ijkl} - A^{+}_{ijkl}\right\}$$
$$= -\,\mathrm{Im}(A - B)_{ijkl} \qquad (2\text{-}35)$$

Thus we find that a complete singlet hessian consists of matrix elements of second order variations with respect to real components of λ, and imaginary components of λ, including complex variations which contains mixed components. Our optimization procedure at the moment makes use of only real variations of the singlet block and utilise only equation (2-28) to obtain the hessian. Explicit expression for the hessian elements are included in appendix 1.

The complete hessian is blocked according to each type of spin symmetry variations such as singlet, triplet, etc. However, since we want to retain the singlet of the ground state, we do not use other blocks of the hessian. This restriction sometimes leads to problems regarding RPA calculations where instabilities occur in generating triplet excitation energies. In the same way one can block the hessian according to spatial symmetries such as , sey, Σ, Π etc. for linear molecules, and S, P etc. for atoms. A variation of the sigma type retains the original symmetry of the molecule in its reference state, which is usually a sigma state. Other types of variations will produce an optimized state with its symmetry corresponding to the cross

product of the symmetry of the infinitesimal generators and that of the reference state. For example, generators of B symmetry acting on a sigma reference state would produce a E state. Since we only optimize our reference with respect to the sigma generators, 'instabilities' in non-sigma blocks of the propagator matrix may occur in calculations indicating that symmetry broken solutions are possible with lowering of energy.

The Excited States Of The GAGP

The excitation energies and the excited states of the GAGP are obtained by the excitation operators as discussed before, and a particular set of N-particle operators known as the diagonal operators. The basis set $\{g^+, g\}$ of one particle excitation operators may be defined to be the following,

$$q_{ij}^{(s)+} = N\, g_j \left(a_i^+ a_j + a_{\bar{i}}^+ a_{\bar{j}}\right) - g_i\left(a_j^+ a_i + a_{\bar{j}}^+ a_{\bar{i}}\right)$$

$$q_{ij}^{(t)+} = N\, g_j \left(a_i^+ a_j - a_{\bar{i}}^+ a_{\bar{j}}\right) + g_i\left(a_j^+ a_i - a_{\bar{j}}^+ a_{\bar{i}}\right) \qquad (2\text{-}36)$$

where the normalization constant N is given by,

$$N = \left(2(\nu_j - \nu_i)(N_j - N_i)\right)^{1/2} \qquad (2\text{-}37)$$

where,

$$\nu_i = g_i^2 \, ; \quad N_i = \langle 0|a_i^\dagger a_i + a_{\bar{i}}^\dagger a_{\bar{i}}|0\rangle \qquad (2\text{-}38)$$

The N-particle diagonal operators are essential for totally symmetric singlet excitations. These operators are of the following form :

$$Q_{ii}^\dagger = \left(a_i^\dagger a_i - \langle a_i^\dagger a_i\rangle\right)|0\rangle\langle 0| \qquad 1 \leq i \leq k \qquad (2\text{-}39)$$

The superscripts s,t in (2-35) refer to singlet and triplet symmetries. Since one may not excite into an IPP(occupied) spinorbital the indices i and j are such that $1 \leq i \leq k$, and $1 \leq j \leq N$, and $g_j = 1$, for $2k+1 \leq j \leq N$ and $g_i = 0$, for $2k+1 \leq i \leq N$. The adjoints of operators annihilate the reference state, ie.,

$$q_{ij}^{(s)}|GAGP\rangle = 0 \qquad \text{for all possible } i,j$$
$$q_{ij}^{(t)}|GAGP\rangle = 0 \qquad (2\text{-}40)$$

While in practice, an exact propagator calculation using a complete set of operators is unfeasible, certain significant properties inherent in the optimised GAGP function allow meaningful interpretation of the propagator with the above truncated set of operators. Weiner [43] has proved that, when a reference state satisfies the following relations,

$$\langle Ref|[H, X^{+}Y]|Ref\rangle = 0 \tag{2-41}$$

and

$$\langle Ref|[H, X]|Ref\rangle = 0 \tag{2-42}$$

For all operators X, Y belonging to an operator subset {V}, it is possible to construct a projected(model) hamiltonian superoperator, $\hat{PHP}$, which acting on the entire hilbert space of operators, leaves the subspace spanned by the basis set of V invariant. In such a case the eigenvectors and eigenvalues obtained by the action of $\hat{PHP}$ and the full hamiltonian on all such operators X, Y are identical. If the reference state is a GAGP, the projection operator is defined as,

$$P = \sum_{i,j,k,l} q_{ij}^{+}|GAGP\rangle\langle GAGP|qq^{+}|GAGP\rangle^{-1}\langle GAGP|q_{kl} + |GAGP\rangle\langle GAGP| \tag{2-43}$$

The GAGP function does not satisfy the relations,

$$\langle GAGP|[H, q_{ij}^{+}q_{kl}^{+}]|GAGP\rangle = 0$$
$$\langle GAGP|[H, q_{ij}q_{kl}^{+}]|GAGP\rangle = 0$$
$$\langle GAGP|[H, q_{ij}q_{kl}]|GAGP\rangle = 0 \tag{2-44}$$

However, the optimized GAGP function does satisfy the generalized Brillouin condition,

$$\langle GAGP|[H,q^{+}]|GAGP\rangle = \langle GAGP|[H,\ q]|GAGP\rangle = 0 \qquad [2\text{-}45]$$

and a very significant relation that was proved by Jensen, Weiner and Ohrn [27], and Sangfelt, Goscinski, Kurtz and Elander [44], is,

$$\langle GAGP|q_{ij}q_{kl}^{+}H|GAGP\rangle = \delta_{ik}\delta_{jl}\langle GAGP|H|GAGP\rangle \qquad (2\text{-}46)$$

A consequence of the GAGP fulfilling relations (2-45), (2-46), is that if the following propagators are constructed, based on the full hamiltonian (2-47), and the model hamiltonian (2-48],

$$G = \begin{bmatrix} \langle GAGP|[q,[H,q^{+}]]|GAGP\rangle & \langle GAGP|[q,[H,q]]|GAGP\rangle \\ \langle GAGP|[q^{+},[H,q^{+}]]|GAGP\rangle & \langle GAGP|[q^{+},[H,q]]|GAGP\rangle \end{bmatrix} \qquad (2\text{-}47)$$

$$G' = \begin{bmatrix} \langle GAGP|[q,[PHP,q^{+}]]|GAGP\rangle & \langle GAGP|[q,[PHP,q]]|GAGP\rangle \\ \langle GAGP|[q^{+},[PHP,q^{+}]]|GAGP\rangle & \langle GAGP|[q^{+},[PHP,q]]|GAGP\rangle \end{bmatrix} \qquad [2\text{-}48]$$

the diagonal blocks of G and G' are identical, so that the generalized TDA based on a model hamiltonian is the same as that based on the full hamiltonian. The subset of operators used to construct the GTDA fulfills conditions expressed by (2-41,2-42). Consequently, it follows that if we consider the excitation operators for the full GRPA,

$$Q_k^+ = \sum_{i,j} \left(Z_{ij,k} q_{ij}^+ + Y_{ij,k} q_{ij} \right) \tag{2-49}$$

the lack of fulfillment of equations (2-41,2-42,2-44) can be attributed to the Y-component of Q^+ in equation (2-49). These components contribute to the construction of the B-block (off diagonal blocks) of the propagator. The generalized TDA has been applied to a range of chemical systems [32], with promising results. The extent of contribution due to the Y-component has been tested on LiH, Li_2, and Be. The results, which comprise the fourth chapter indicate that the norm of the vector Y is virtually zero for these systems. This is reassuring in establishing GAGP as a good reference state for the Polarization Propagator.

CHAPTER THREE
OPEN SHELL GAGP

Functional Form

For simplicity we will concern ourselves, in this chapter, with reference states that have a single unpaired electron. Examples of this type are alkali metal atoms such as lithium, sodium etc. and molecules such as CH, ArH etc. Certain doublet excited states of the nitrogen atom may also qualify as a reference state for that system. Without loss of generality we will consider our reference function to have $m_s = +1/2$. For clarity and convenience we will represent the orbital which is singly occupied in the reference state by ϕ_o. The open shell GAGP reference state is of the following form:

$$|GAGP\rangle = (C\sqrt{N-2k})^{-1}\, O_{AS}(G^{+})^{k}(\phi^{+}_{2k+1}\phi^{+}_{\overline{2k+1}} \cdots \phi^{+}_{\overline{N-1}}\phi^{+}_{o})|vac\rangle \tag{3-1}$$

The calculation and the optimization of the reference state require the same formalism as in the closed shell case. The only minor difference occurs in the construction of the two matrix, where the diagonal element in the D-block, corresponding to ϕ_o is zero, and all terms in the C-block using ϕ_o are also zero. Also while using equation (2-23) for obtaining the gradient elements and equations (2-29) to obtain the hessian elements, variations involving ϕ_o are obviously zero.

Single particle excitations out of the doublet reference state may generate either a pure or mixed spin states which are the following:

1) A singlet excitation operator generates a doublet state,

2) a triplet excitation operator, yielding $\Delta m_s = 0$, generates a mixture of doublet and quartet states of $m_s = 1/2$,

3) a triplet excitation operator, yielding $\Delta m_s = 1$, will generate a pure quartet state with $m_s = 3/2$,

4) a triplet excitation operator, producing $\Delta m_s = -1$, will generate mixed doublets and quartets of $m_s = -1/2$.

While one could choose case 1) and 3) to obtain pure spin states an additional complication arises for doublet excited states. A singlet excitation operator will essentially generate three unpaired electrons out of the open shell GAGF (3-1), with $m_s = 1/2$. In such a case, the doublet manifold is two-dimensional [45], and any linear combinations of two linearly independent spin functions from this space are eigenfunctions of S^2. Either a branching diagram scheme [45] or Young Tableaux diagrams [46] may be used to construct the proper eigenfunctions. Possible functions that span the spin space are

$$1)\ \Phi_{ij,1} = |\phi_o\phi_{\bar{i}}\phi_j| - |\phi_o\phi_{\bar{j}}\phi_i| \qquad (3\text{-}2a)$$

$$2)\ \Phi_{ij,2} = 2|\phi_{\bar{o}}\phi_i\phi_j| - |\phi_o\phi_{\bar{i}}\phi_j| - |\phi_o\phi_{\bar{j}}\phi_i| \qquad (3\text{-}2b)$$

For all possible i,j

The above functions adequately illustrate the situation for the formation of excited states since the full excited state may be constructed by an antisymmetrized product of the $|GAGP\rangle$ (3-1), with orbitals ϕ_o, ϕ_i, and ϕ_j deleted from it, and an appropriate combination of the above functions, (3-2a) and (3-2b). It is at once realized that our singlet excitation operator used in the previous chapter, equation (2-38), when allowed to act on the restricted doublet GAGP reference will yield (3-2a). Furthermore, it is also quite readily seen that the second function (3-2b) cannot be obtained by any one particle excitation operator from the same reference state, since the first determinant in (3-2b) require simultaneous replacement of two spin orbitals by two others which include replacing ϕ_o by $\phi_{\bar{o}}$. In order to have functions of the form (3-2b), we need to introduce a new set of excitation operators that include certain types of two particle operators. Thus the excitation operators required to obtain the two sets of doublets are of the type,

$$1)\quad Q_{ij}^{(D_1)+} = g_j(a_i^+a_j + a_{\bar{i}}^+a_{\bar{j}}) - g_i(a_j^+a_i + a_{\bar{j}}^+a_{\bar{i}}) \qquad (3\text{-}3a)$$

$$\begin{aligned} 2)\quad Q_{ij}^{(D_2)+} &= 2g_j(a_{\bar{o}}^+a_o a_i^+a_{\bar{j}}) + 2g_i(a_{\bar{o}}^+a_o a_{\bar{j}}^+a_i) \\ &\quad - g_j(a_i^+a_j - a_{\bar{i}}^+a_{\bar{j}}) - g_i(a_j^+a_i - a_{\bar{j}}^+a_{\bar{i}}) \qquad (3\text{-}3b) \end{aligned}$$

The triplet excitation operator which produces the high spin quartet ($m_s = 3/2$), is of the following form,

$$Q_{ij}^{(q)+} = g_j\ a_i^+ a_{\bar{j}} + g_i\ a_j^+ a_{\bar{i}} \tag{3-4}$$

Before launching into the algebra of this new set of operators let us investigate the possibility of not incorporating the second doublet function (3-2b). The hamiltonian expectation value between two functions from the sets containing the functions (3-2a,3-2b) is

$$\langle H \rangle_{abcd} = \langle \psi_{ab,2} | \hat{H} | \psi_{cd,1} \rangle = \langle \psi_{cd,1} | \hat{H} | \psi_{ab,2} \rangle$$
$$\neq 0 \tag{3-5}$$

which may be proved using the second quantized operators. We have in particular, that

$$\langle GAGP | \Big(g_a (2a_o^+ a_b^+ a_a a_{\bar{o}} - (a_b^+ a_a - a_{\bar{b}}^+ a_{\bar{a}})) - g_b (2a_o^+ a_{\bar{b}}^+ a_a a_{\bar{o}} -$$
$$(a_b^+ a_a - a_{\bar{b}}^+ a_{\bar{a}})) \Big)\ K_H \Big(g_c (a_d^+ a_c + a_{\bar{d}}^+ a_{\bar{c}}) - g_d (a_c^+ a_d + a_{\bar{c}}^+ a_{\bar{d}})) \Big) | GAGP \rangle$$

$$= \sum_{i,j,k,l} \Big((N-1)^{-1} (h_{ik} \delta_{jl} - h_{il} \delta_{jk} - h_{jk} \delta_{il} + h_{jl} \delta_{ik}) + \langle ij || kl \rangle \Big) \times$$

$$\langle GAGP | \Big(g_a (2a_c^+ a_{\bar{b}}^+ a_a a_{\bar{o}} - (a_b^+ a_a - a_{\bar{b}}^+ a_{\bar{a}})) - g_b (2a_o^+ a_{\bar{b}}^+ a_a a_{\bar{o}} -$$
$$(a_b^+ a_a - a_{\bar{b}}^+ a_{\bar{a}})) \Big) a_i^+ a_j^+ a_l a_k \Big(g_c (a_d^+ a_c + a_{\bar{d}}^+ a_{\bar{c}}) - g_d (a_c^+ a_d + a_{\bar{c}}^+ a_{\bar{d}})) \Big) | GAGP \rangle$$

$$= g_a g_c \{ \langle \bar{o}a || \bar{d}o \rangle (\langle GAGP | a_o^+ a_{\bar{b}}^+ a_{\bar{c}} a_o + a_o^+ a_{\bar{b}}^+ a_{\bar{d}}^+ a_{\bar{d}} a_{\bar{c}} a_o + a_o^+ a_{\bar{b}}^+ a_a^+ a_a a_{\bar{c}} a_o$$
$$- a_o^+ a_{\bar{b}}^+ a_a^+ a_{\bar{d}}^+ a_{\bar{d}} a_a a_{\bar{c}} a_o | GAGP \rangle \delta_{\bar{b}\bar{c}})$$
$$+ \langle \bar{o}c || \bar{b}o \rangle (\langle GAGP | a_o^+ a_{\bar{b}}^+ a_c^+ a_c a_{\bar{b}} a_o - a_o^+ a_{\bar{b}}^+ a_c^+ a_d^+ a_a a_c a_{\bar{b}} a_o | GAGP \rangle \delta_{ad}) \}$$
$$- g_b g_c \{ \langle \bar{o}b || \bar{d}o \rangle (\langle GAGP | a_o^+ a_{\bar{a}}^+ a_{\bar{c}} a_o + a_o^+ a_{\bar{a}}^+ a_{\bar{d}}^+ a_{\bar{d}} a_{\bar{c}} a_o + a_o^+ a_{\bar{a}}^+ a_b^+ a_b a_{\bar{c}} a_o$$
$$+ a_o^+ a_{\bar{a}}^+ a_b^+ a_{\bar{d}}^+ a_{\bar{d}} a_b a_{\bar{c}} a_o | GAGP \rangle \delta_{\bar{a}\bar{c}})$$
$$- \langle \bar{o}c || \bar{a}o \rangle (\langle GAGP | a_o^+ a_{\bar{a}}^+ a_c^+ a_c a_{\bar{a}} a_o - a_o^+ a_{\bar{a}}^+ a_c^+ a_d^+ a_b a_c a_{\bar{a}} a_o | GAGP \rangle \delta_{bd}) \}$$
$$- g_a g_d \{ \langle \bar{o}a || \bar{c}o \rangle (\langle GAGP | a_o^+ a_{\bar{b}}^+ a_{\bar{d}} a_o + a_o^+ a_{\bar{b}}^+ a_{\bar{c}}^+ a_{\bar{c}} a_{\bar{d}} a_o + a_o^+ a_{\bar{b}}^+ a_a^+ a_a a_{\bar{d}} a_o$$
$$+ a_o^+ a_{\bar{b}}^+ a_a^+ a_{\bar{c}}^+ a_{\bar{c}} a_a a_{\bar{d}} a_o | GAGP \rangle \delta_{\bar{b}\bar{d}})$$
$$- \langle \bar{o}d || \bar{b}o \rangle (\langle GAGP | a_o^+ a_{\bar{b}}^+ a_d^+ a_d a_{\bar{b}} a_o - a_o^+ a_{\bar{b}}^+ a_d^+ a_c^+ a_a a_d a_{\bar{b}} a_o | GAGP \rangle \delta_{ac}) \}$$
$$+ g_b g_d \{ \langle \bar{o}b || \bar{c}o \rangle (\langle GAGP | a_o^+ a_{\bar{a}}^+ a_{\bar{d}} a_o + a_o^+ a_{\bar{a}}^+ a_{\bar{c}}^+ a_{\bar{c}} a_{\bar{d}} a_o + a_o^+ a_{\bar{a}}^+ a_b^+ a_b a_{\bar{d}} a_o$$
$$- a_o^+ a_{\bar{a}}^+ a_b^+ a_{\bar{c}}^+ a_{\bar{c}} a_b a_{\bar{d}} a_o | GAGP \rangle \delta_{\bar{a}\bar{d}})$$
$$+ \langle \bar{o}d || \bar{a}o \rangle (\langle GAGP | a_o^+ a_{\bar{a}}^+ a_d^+ a_d a_{\bar{a}} a_o - a_o^+ a_{\bar{a}}^+ a_d^+ a_c^+ a_b a_d a_{\bar{a}} a_o | GAGP \rangle \delta_{bc}) \} \quad (3\text{-}6)$$

for all g_a, g_b, g_c, and g_d. In order for equation (3-6) to be zero, either all the two electron integrals must be zero or all the second, third and fourth order density matrix elements left after evaluation of the kronecker delta functions must vanish, or the products must cancel. This is not in general possible as these density matrix elements are precisely those which are non-zero (see chapter two) and the integrals vary from problem to problem. Equation (3-6) is therefore in general non-zero. The above proof implies that the hamiltonian is not block diagonalized according to each set of functions $\{\psi_1\}$, $\{\psi_2\}$. True excited states obtained by

diagonalizing the hamiltonian matrix of the above type would then in general be a linear combination of the functions ψ_1 and ψ_2. If the two sets of functions did not interact through the hamiltonian, then each set of eigenvalues and eigenfunction, obtained by diagonalizing the hamiltonian would be independent of the other set. This would have meant losing certain eigenvalues by not considering both sets but not effect the exactness of the results. Because of equation (3-4), eigenvectors obtained with any one set of operators will not necessarily correspond to proper excited states of the system.

GTDA And GRPA For Doublet Excited States

Obtaining the quartet excited states is quite similar to obtaining triplet excited states in the case of singlet reference states and therefore will not be included in the following discussions. To carry out a GTDA calculation for the doublet states we will need to consider the following the types of integrals,

1) $\langle GAGP|[Q^{(D_1)}, [H_H, Q^{(D_1)+}]]|GAGP\rangle$ (3-7)

2) $\langle GAGP|[Q^{(D_1)}, [H_H, Q^{(D_2)+}]]|GAGP\rangle$ (3-8)

3) $\langle GAGP|[Q^{(D_2)}, [H_H, Q^{(D_1)+}]]|GAGP\rangle$ (3-9)

4) $\langle GAGP|[Q^{(D_2)}, [H_H, Q^{(D_2)+}]]|GAGP\rangle$ (3-10)

The excitation energies may be obtained by diagonalizing the entire matrix. While reviewing the consistency of the GTDA, the following problems are encountered. In order that we may exclude the reference state from our excited state calculations, the excited states generated by (3-3a) and (3-3b) must satisfy the generalized Brillouin condition, ie

$$\langle GAGP | [K_H\ ,\ C_1 Q^{(D_1)+} + C_2 Q^{(D_2)+}]] | GAGP \rangle = 0 \qquad (3\text{-}11)$$

where C_1 and C_2 are expansion coeffients corresponding to excited states. The stationarity condition imposed on the GAGP in obtaining the optimized reference state ensures that it satisfies the generalized Brillouin condition with respect to the first doublet excitation operator, ie

$$\langle GAGP | [K_H\ ,\ Q^{(D_1)+}] | GAGP \rangle = 0 \qquad (3\text{-}12)$$

which then leaves us to enquire if

$$\langle GAGP | [K_H\ ,\ Q^{(D_2)+}] | GAGP \rangle = 0 \qquad (3\text{-}13)$$

Expanding the left-hand side of (3-13), we obtain

$$\langle GAGP|\Big[\sum_{\substack{i,j,\\k,l}} \langle ij||kl\rangle a_i^{+}a_j^{+}a_l a_k \,,\, g_b\Big\{2a_{\bar{o}}^{+}a_{o}^{+}a_{\bar{b}}a_{b} - \big(a_a^{+}a_b - a_{\bar{a}}^{+}a_{\bar{b}}\big)\Big\}$$

$$+\ g_a\Big\{2a_{\bar{o}}^{+}a_{b}^{+}a_{\bar{a}}a_{a} - \big(a_b^{+}a_a - a_{\bar{b}}^{+}a_{\bar{a}}\big)\Big\}\Big]|GAGP\rangle$$

$$= 4\ g_b\langle a\bar{b}||a\bar{o}\rangle \langle GAGP|a_c^{+}a_{\bar{b}}^{+}a_a^{+}a_a a_{\bar{b}}a_o - a_o^{+}a_{\bar{b}}^{+}a_{\bar{b}}a_o|GAGP\rangle$$

$$+\ 4\ g_a\langle o\bar{a}||b\bar{o}\rangle \langle GAGP|a_c^{+}a_{\bar{a}}^{+}a_b^{+}a_b a_{\bar{a}}a_c - a_o^{+}a_{\bar{a}}^{+}a_{\bar{a}}a_o|GAGP\rangle$$

$$\neq\ 0 \tag{3-14}$$

Since the generalised Brillouin condition is not satisfied, a GTDA calculation would be pointless unless the optimised GAGP function was included in the propagator matrix for obtaining excited states. This would essentially lead to no identifiable and well defined reference state. This lack of any formal consistency leads us to look for better approximations.

We have considered two different methods of approaching this open shell calculation using the GAGP formalism. 1) The first one is to construct the entire generalised RPA matrix using excitation operators (3-3a and 3-3b). The results of the GRPA should be comparable to those of the typical RPA calculations based on an AGP. The necessary propagator elements for this approach have been derived but still need to be computer coded. The matrix elements are included in Appendix 2. 2) In the second approach, a consistent GTDA is constructed using only the first set of doublets $\{\psi_1\}$. These states fulfil all the conditions that were outlined for closed shell GTDA case in the previous chapter. It is assumed that the mixing of the two sets of functions $\{\psi_1\}$

and $\{\psi_2\}$ is small and that the eigenvalues and eigenvectors will not be affected too much by this approximation. In this particular formalism, we need to include in the set of excitation operators $\{Q^+_{ij}(D_1)\}$, of equation (3-3a), the excitation operator Q^+_{oj}, which involves excitations of the open shell spin orbital.

$$Q_{oj}^{(D_1)+} = (1-(1-\nu_j)N_j/2)^{1/2}(a_j^+a_a - g_j a_{\bar{a}}^+ a_{\bar{j}}) \qquad 1 \leq j \leq k \qquad (3\text{-}15a)$$

$$Q_{oa}^{(D_1)+} = a_o^+ a_{\bar{a}} \qquad 2k+1 \leq a \leq e \qquad (3\text{-}15b)$$

The adjoints of the above operators annihilate the GAGF function.

We applied GTOA to the Li atom, using a 5s 2p GTO basis set [48] and a larger basis set, obtained by augmenting the the basis set with a diffused d Gaussian type function. The results for the first three excitation energies are presented. We compare our results with experimental findings [47], and also other theoretical calculations, using the propagator approach. These include calculations by Swenstrøm and Jørgensen [19], who have used 50 STO's to evaluate the first seven excitation energies. They have used both the HF-RPA (TDHF), and the second order polarization propagator approach (SOPPA) to obtain their results. In the SOPPA calculation, the two-particle two-hole propagator elements required in the generation of the degenerate set of doublet

states (3-2b), are incorporated as a second order perturbative correction to the TDHF. The results indicate the effect of this correction to be quite small. The first three excitation energies calculated by AGF-TDA are quite accurate. However to obtain higher excitation energies one must use larger basis sets. The higher ^2S excitation energies can also be further improved by the inclusion of the N-particle diagonal operators, equation (2-41), which is now in the process of being coded. Tables 1 and 2 present the basis sets used, and table 3 contain the Li results.

TABLE 1. Li Basis (1)

11 CGTO Basis

Type	Exponent	Coefficient
Li,s	921.300	0.001367
	138.700	0.010425
	31.9400	0.049859
	9.353	0.160701
	3.158	0.344604
	1.1570	0.425197
Li,s	0.4446	1.00000
Li,s	0.07666	1.00000
Li,s	0.02664	1.00000
Li,p	1.488	0.03877
	0.2667	0.236257
	0.07201	0.830448
Li,p	0.0237	1.00000

TABLE 2 Li Basis (2)

16 CGTO Basis

Type	Exponent	Coefficient
Li,s	921.300	0.001367
	138.700	0.010425
	31.9400	0.049859
	9.353	0.160701
	3.158	0.344604
	1.1570	0.425197
Li,s	0.4446	1.00000
Li,s	0.07666	1.00000
Li,s	0.02864	1.00000
Li,p	1.488	0.03877
	0.2667	0.236257
	0.07201	0.830448
Li,p	0.0237	1.00000
Li,d	0.1500	1.00000

TABLE 3 Li Atom Excitation Energies (ev)

	$2p\ ^2P$	$3s\ ^2S$	$3p\ ^2P$
AGP-TDA(s)	1.852	3.306	4.100
AGP-TDA(1)	1.863	3.305	4.111
TDHF	1.827	3.334	3.795
SOPPA	1.834	3.348	3.800
EXPT.	1.847	3.372	3.833

CHAPTER FOUR
AGP-TDA, AGP-RPA BASED RESULTS AND CONCLUSIONS

Potential energy surfaces for ground and excited states, and other spectroscopic properties such as transition moments, and radiative lifetimes for LiH and Li_2 have already been successfully produced by AGP-TDA [44,49]. There is virtually complete agreement of the shapes of curves produced by AGP-TDA for LiH with extensive MCSCF calculations [50]. The Li_2 results are also very impressive and compare well with experimental findings as well as the leading theoretical calculations [references in [49]]. However, the strength of AGP as a reference function would not be fully understood without similar calculations using AGP-RPA. The contributing terms of the "A" block (following the notation from chapter one) are the following

$$1)\ \langle 0|q_{ij}Hq^{+}_{kl}|0\rangle \qquad \text{for all possible } i,j,k,l \qquad (4\text{-}1)$$

$$2)\ \langle 0|q_{ij}q^{+}_{kl}H|0\rangle$$

The first term is the hamiltonian expectation value between two single particle excitations out of the GAGP. The second term, by virtue of the equality that was proved by Jensen, Weiner and Ohrn [27] and Sangfelt, Kurtz, Elander and Goscinski [44], is a constant quantity and is equal to the reference state energy for the diagonal elements and zero

for the others. The AGP-TDA (which is equivalent to evaluating the A block of the propagator) is therefore essentially a mono-excited CI matrix which on diagonalization will yield energy differences between ground and excited states (which are also eigenstates of the hamiltonian). The contribution to the B block of the propagator arises from the following term :

1) $\langle 0|q_{ij}q_{kl}H|0\rangle$ (4-2)

which represents interaction of the reference state with two particle excitations out of the reference through the hamiltonian. The B block which is included in the RPA matrix constitutes a measure of the contamination of the reference into the excited states. In the following sections the comparative results for AGP-TDA and AGP-RPA for LiH, Li_2 and Be atom are presented together with similar calculations based on a HF reference state. Since the computer codes for evaluating the diagonal operators have not been developed yet for the RPA scheme we have excluded those from TDA calculations as well for proper comparisons.

Potential Energy Surfaces (LiH and Li_2)

The low lying singlet and triplet excited states together with the reference are portrayed in figures 1-8. For both systems, AGP based TDA and RPA do not exhibit any

detectable difference, and for each state the curves are completely superimposed. The weakly bound (a well of .035 ev) characteristic of the X $^1\Sigma$ state of LiH, as predicted by experiments [51], is not yielded by the AGP with this basis set. However, the HF-RPA, HF-TDA predicts quite a deep well of 1.5 ev. While both singlet excited state curves of LiH in the HF picture seem to rise at large internuclear distances, the shape of the A $^1\Sigma^+$ is slightly improved by the HF-RPA. The 2 $^3\Sigma$ and 3 $^3\Sigma$ of LiH are predicted to have avoided crossings by both AGP and HF, however the HF-RPA calculations run into a serious stability problem for the triplet states (discussed in chapters one and two) and the 1 $^3\Sigma$ state breaks down completely. An identical trend is observed for the Li_2 molecule. The shape of the A $^1\Sigma_u^+$ state is slightly improved as before by the HF-RPA over HF-TDA. The triplet instabilities are just as pronounced for Li_2 as in LiH and as a result of this the HF-RPA curve for the b $^3\Sigma_u$ state cannot be plotted. Thus, comparing AGP and HF results for the triplet states show that a remarkable improvement has been achieved for the AGP regarding stability. We also present in tables 6 and 7, numerical results indicating the effect of the RPA in comparison to TDA. In these tables ω denotes the excitation energy between the ground and excited states.

TABLE 4. LiH Basis

3D CGTO Basis

Type	Exponent	Coefficient
Li,s	642.4189	0.00214
	96.79849	0.01621
	22.09109	0.07732
	6.20107	0.24579
	1.93512	0.47019
	0.63674	0.34540
Li,s	2.19146	0.003509
	0.59613	0.19123
Li,s	0.07455	1.00000
Li,s	0.02867	1.00000
Li,s	0.00920	1.00000
Li,p	2.19146	0.00894
	0.59613	0.14101
	0.07455	0.94535
Li,p	0.01000	1.00000
H,s	837.22	0.000112
	123.524	0.000895
	27.7042	0.000895
	2.56504	0.065862
	0.938250	0.178000
H,s	0.372145	1.00000
H,s	0.155838	1.00000
H,s	0.06618	1.00000
H,p	2.1175	1.00000
H,p	0.77	1.00000
H,p	0.28	1.00000
H,d	1.00000	1.00000

TABLE 5. Li_2 BASIS

32 CGTO Basis

Type	Exponent	Coefficient
Li,s	921.300	0.001367
	138.700	0.010425
	31.9400	0.049859
	9.353	0.160701
	3.158	0.344604
	1.1570	0.425197
Li,s	0.4446	1.00000
Li,s	0.07666	1.00000
Li,s	0.02864	1.00000
Li,p	1.488	0.03877
	0.2687	0.236257
	0.07201	0.830448
Li,p	0.0237	1.00000
Li,d	0.1500	1.00000

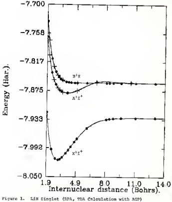

Figure 1. LiH Singlet (RPA, TDA Calculation with AGP)

· TDA Calculation

+ RPA Calculation

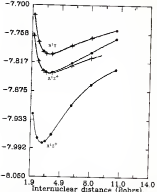

Figure 2. LiH Singlet States (RPA, TDA Calculation with HF)

• TDA Calculation

+ RPA Calculation

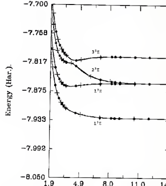

Figure 3. LiH Triplet States (RPA, TDA Calculation with AGP)

· TDA Calculation

+ RPA Calculation

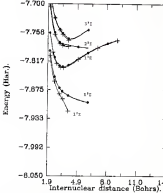

Figure 4. LiH Triplet States (RPA, TDA Calculation with HF)

· TDA Calculation

+ RPA Calculation

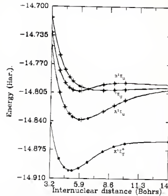

Figure 5. Li_2 Singlet States (RPA, TDA Calculation with AGP)

· TDA Calculation

\+ RPA Calculation

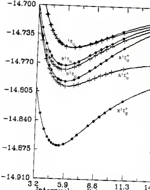

Figure 6. Li_2 Singlet States (RPA, TDA Calculation with HF)

· TDA Calculation

\+ RPA Calculation

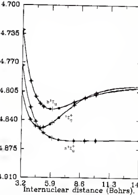

Figure 7. Li_2 Triplet States (RPA, TDA Calculation with AGP)

· TDA Calculation

\+ RPA Calculation

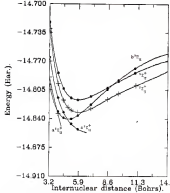

Figure 8. Li_2 Triplet States (RPA, TDA Calculation with HF)

· TDA Calculation

\+ RPA Calculation

As pointed out in chapter two, the contribution of the 'B' block of the RPA is proportional to the norm of the vector Y, (2-51). We therefore estimate the extent of consistency of the AGP reference state by 1) the smallness of the vector Y and the 2) the relative magnitude of matrices 'A' and 'B' ie the magnitude of the ratio of the traces of the squares of matrices A and B. This ratio indicates that the dominant (diagonal) contributions of the 'A' block are several orders of magnitude higher than those of the 'B'. For LiH, this ratio is larger in AGP than in HF for all the symmetry blocks. The results, though tabulated only for the equilibrium geometry of the ground state, are typical of the entire surface. The norm of the vector Y is virtually vanishing for the AGP indicating in these cases that the AGP is indeed a consistent reference function. It is interesting to note that the $^1\Sigma_u^+$ state of Li_2 has the ratio of the traces of the squares of A and B, larger for HF than for AGP, which suggests that the relative contribution of B matrix is smaller in HF for this symmetry block. However the norm of Y vector in AGP is much smaller, which is also reflected in the agreement of the plotted AGP-TDA, AGP-RPA curves.

TABLE 6. Comparison Of

AGP-RPA, HF-RPA For LiH At 3.1 Bohrs

Type	ω(ev)	Z^+Z	Y^+Y	$\frac{\text{Tr. Sq. A}}{\text{Tr. Sq. B}}$
1 $^3\Sigma$				
AGP	3.12	1.000008	0.000008	3.23×10^4
HF	2.65	1.051621	0.051621	2.95×10^3
2 $^3\Sigma$				
AGP	5.52	1.000001	0.000001	3.23×10^4
HF	5.41	1.008106	0.008106	2.95×10^3
3 $^3\Sigma$				
AGP	6.04	1.000001	0.000001	3.23×10^4
HF	6.19	1.003411	0.003411	2.95×10^4
A $^1\Sigma^+$				
AGP	3.91	1.000003	0.000003	2.22×10^4
HF	3.97	1.003289	0.003289	3.00×10^3
1 $^3\Pi$				
AGP	4.23	1.000002	0.000002	2.08×10^7
HF	4.15	1.006825	0.006825	1.43×10^4
B $^1\Pi$				
AGP	4.58	1.000003	0.000003	1.25×10^7
HF	5.04	1.001855	0.001855	1.43×10^4

TABLE 7. Comparison Of

AGP-RPA, HF-RPA For Li_2 At 5.1 Bohrs

Type	ω(ev)	Z^+Z	Y^+Y	$\frac{\text{Tr. Sq. A}}{\text{Tr. Sq. B}}$
a $^3\Sigma_g^+$				
AGP	1.27	1.000013	0.000013	4.73×10^3
HF	Instab.			
$^3\Sigma_u^+$				
AGP	2.13	1.000003	0.000003	4.04×10^3
HF	1.11	1.177032	0.177032	1.70×10^3
A $^1\Sigma_u^+$				
AGP	1.62	1.000017	0.000017	2.24×10^2
HF	2.06	1.027820	0.027820	1.79×10^3
b $^3\Pi_u$				
AGP	1.40	1.000002	0.000002	6.69×10^5
HF	Instab.			
B $^1\Pi_u$				
AGP	2.70	1.000006	0.000006	3.52×10^5
HF	2.55	1.026277	0.026277	1.06×10^4
$^1\Pi_g$				
AGP	3.03	1.000005	0.000005	5.38×10^5
HF	3.43	1.001538	0.001538	5.37×10^4

Transition Moments

The lifetime of electronic excitations is a particularly useful quantity since it cannot be measured experimentally very easily. For the calculation of lifetimes one needs to know the electronic transition moments, and these are quite easily calculated in the propagator formalism [44]. The transition dipole M_{0k} between the ground and an excited state k, is given by

$$M_{0k} = \langle 0|r|k\rangle \tag{4-4}$$

where r is the dipole length vector. Equation (4-4) may be rewritten using the excitation operators as

$$M_{0k} = \sum_{i>j} C^k_{ij} \langle 0|r\, Q^+_{ij}|0\rangle \tag{4-5}$$

$$= \sum_{i>j} C^k_{ij} \langle 0|[r\, Q^+_{ij}]|0\rangle \tag{4-6}$$

where C^k_{ij} are expansion coefficients for state k. Equation (4-6) is possible when the vacuum condition is satisfied. We may express the dipole vector r as

$$r = \sum_{m>n} r_{mn}(Q^+_{mn} - Q_{mn})(g_n - g_m)^{-\lambda} \tag{4-7}$$

where r_{mn} is the dipole element between orbitals m and n. Substitution of (4-7) into (4-6) leads to a very simple expression for the transition moment,

$$M_{0k} = \sum_{i>j} C_{ij}^{k} r_{ij} [(\upsilon_j - \upsilon_i)(N_j - N_i)]^{-1/2} (g_j - g_i) \tag{4-8}$$

We only calculate the ground-excited state dipole moments and not excited-excited state dipole moments. The excited-excited state transitions can also be handled in the AGP-TDA formalism, but one might question the corresponding RPA calculations since the excited states are only well-defined when the B-matrix is small. The shapes of the LiH and Li_2 transition moment curves are in excellent agreement with other leading MCSCF calculations, whereas the HF results are quite inadequate, even though the HF-RPA is somewhat better than the HF-TDA.

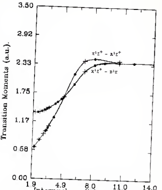

Figure 9. LiH Transition Moments (RPA, TDA Calculation with AGP)

· TDA Calculation

+ RPA Calculation

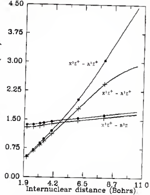

Figure 10. LiH Transition Moments (RPA, TDA Calculation with HF)

• TDA Calculation

+ RPA Calculation

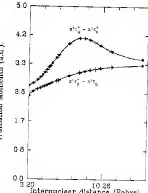

Figure 11. Li_2 Transition Moments (RPA, TDA Calculation with AGP)

· TDA Calculation

+ RPA Calculation

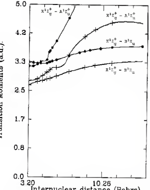

Figure 12. Li_2 Transition Moments (RPA, TDA Calculation with HF)

· TDA Calculation

+ RPA Calculation

Be Results

Using a 6s 3p 2d basis (table 8), we compare the first two excitation energies for S and P symmetries for both singlets and triplets. The agreement of the AGP results with experimental values [52] is rather good and there are no instabilities. The results for ^1S are in fact much improved with the inclusion of diagonal operators, (2-41) and yield an excitation energies of 6.91 and 8.099 ev. The agreement of the AGP-TDA and AGP-RPA is also reflected by the diminutive norm of Y and large ratio of the traces of squares of A and B. The AGP calculation results for transition probability compares very well with experiment [53].

TABLE B. Be Basis

27 CGTO Basis

Type	Exponent	Coefficient
Be,s	1741.000 262.000 60.330 17.6200 5.933 0.859	0.001305 0.009955 0.048031 0.158577 0.351325 0.16049
Be,s	2.185	1.00000
Be,s	0.1606	1.00000
Be,s	0.05835	1.00000
Be,s	0.02900	1.00000
Be,s	0.0020	1.00000
Be,p	6.7100 1.442 0.4103 0.1397	0.016378 0.091553 0.341469 0.685428
Be,p	0.04922	1.00000
Be,p	0.0125	1.00000
Be.d	1.0000	1.00000
Be,d	0.19958	1.00000

TABLE 9.AGP, HF Excitation Energies (ev) For Be (S States)

	AGP		HF		EXP
	TDA	RPA	TDA	RPA	
^3S	6.52	6.52	5.62	5.57	6.45
Y^+Y		0.000003		0.003466	
^3S	6.62	6.02	7.16	7.15	6.00
Y^+Y		0.000000		0.000336	
$\frac{Tr.Sq.A}{Tr.Sq.B}$		$0.79x10^4$		$0.20x10^4$	
^1S	7.05	7.05	6.36	6.34	6.76
Y^+Y		0.000003		0.001006	
^1S	8.13	6.13	7.34	7.33	8.09
Y^+Y		0.000002		0.000439	
$\frac{Tr.Sq.A}{Tr.Sq.B}$		$6.45x10^4$		$0.21x10^4$	

TABLE 10.AGP, HF Excitation Energies (ev) For Be (P States)

	AGP TDA	AGP RPA	HF TDA	HF RPA	EXP
^3P	2.74	2.74	1.70	Inst	2.73
Y^+Y		0.000001			
^3P	7.31	7.31	8.44	6.43	7.29
Y^+Y		0.000000		0.001861	
$\frac{Tr.Sq.A}{Tr.Sq.B}$		$0.12x10^7$		$0.88x10^4$	
^1P	5.48	5.48	5.09	4.84	5.28
Y^+Y		0.000004		0.025328	
^1P	7.48	7.48	8.83	6.77	7.48
Y^+Y		0.000001		0.004299	
$\frac{Tr.Sq.A}{Tr.Sq.B}$		$0.87x10^6$		$0.84x10^4$	

TABLE 11. AGP, BF Results For Be (Transition Moment)

	AGP		BF		EXP
	TDA	RPA	TDA	RPA	
Dip. Tr. Mom.	1.88	1.88	2.26	1.98	
Σ Sq. of Dip. Tr. Mom.	10.60	10.60	15.23	11.76	10.37 ± 0.38

APPENDIX 1
GRADIENT, HESSIAN AND PROPAGATOR ELEMENTS OF CLOSED SHELL GAGP

The different types of gradient elements are,

$$\left[\nabla_\lambda E(0,g)\right]_{kl} = 4 \sum_{j=1}^{s} \Big\{ (K_H)_{kljj} \left[\left(D_a^{(2)}\right)_{jl} - \left(D_b^{(2)}\right)_{kj} \right]$$

$$2\,(K_H)_{kjlj} \left[\left(D_b^{(2)}\right)_{jl} - \left(D_a^{(2)}\right)_{kj} \right] \Big\}$$

$$8 \sum_{j=2s+1}^{\frac{1}{2}(N-2k)} (K_H)_{kjlj} \left[\left(D_c^{(2)}\right)_{jl} - \left(D_c^{(2)}\right)_{kj} \right]$$

for $1 \leq k, l \leq 2s$, and,

$$\left[\nabla_\lambda E(0,g)\right]_{kl} = 8 \sum_{j=1}^{s} \Big\{ (K_H)_{kjlj} \left[\left(D_b^{(2)}\right)_{jl} - \left(D_c^{(2)}\right)_{kj} \right]$$

$$8 \sum_{j=2s+1}^{\frac{1}{2}(N-2k)} (K_H)_{kjlj} \left[\left(D_c^{(2)}\right)_{jl} - I \right\}$$

for $2s+1 \leq k \leq 2s+(N-2k)$ end $1 \leq l \leq s$, and,

$$\left[\nabla_\lambda E(0,g)\right]_{kl} = 0$$

for $2s+1 \leq k, l \leq 2s+(N-2k)$

A hessian element H_{abcd} of a GASP has the following form,

$$H_{abcd} = 16(ab|cd)(\langle 0|a_b^+ a_d^+ a_d a_b + a_a^+ a_c^+ a_c a_a - a_b^+ a_c^+ a_c a_b - a_a^+ a_d^+ a_d a_a|0\rangle$$

$$+ 8((ac|bd) + (ad|bc))(\langle 0|a_b^+ a_c^+ a_c a_b + a_a^+ a_d^+ a_d a_a - a_b^+ a_d^+ a_d a_b - a_a^+ a_c^+ a_c a_a$$

$$+ a_b^+ a_{\bar{b}}^+ a_{\bar{d}} a_d + a_a^+ a_{\bar{a}}^+ a_{\bar{c}} a_c - a_a^+ a_{\bar{a}}^+ a_{\bar{d}} a_d - a_b^+ a_{\bar{b}}^+ a_{\bar{c}} a_c|0\rangle$$

$$- \sum_n \Big\{ 2(nb|nd)(\langle 0|a_n^+ a_{\bar{n}}^+ a_{\bar{b}} a_b + a_n^+ a_{\bar{n}}^+ a_{\bar{d}} a_d - a_n^+ a_b^+ a_b a_n - a_n^+ a_d^+ a_d a_n$$

$$+ 2a_a^+ a_n^+ a_n a_a - 2a_a^+ a_{\bar{a}}^+ a_{\bar{n}} a_n|0\rangle)\delta_{ac}$$

$$+ 2(an|nd)(\langle 0|a_n^+ a_{\bar{n}}^+ a_{\bar{a}} a_a + a_n^+ a_{\bar{n}}^+ a_{\bar{d}} a_d - a_n^+ a_a^+ a_a a_n - a_n^+ a_d^+ a_d a_n$$

$$+ 2a_b^+ a_n^+ a_n a_b - 2a_b^+ a_{\bar{b}}^+ a_{\bar{n}} a_n|0\rangle)\delta_{bc}$$

$$+ 2(nb|cn)(\langle 0|a_n^+ a_{\bar{n}}^+ a_{\bar{b}} a_b + a_n^+ a_{\bar{n}}^+ a_{\bar{c}} a_c - a_n^+ a_b^+ a_b a_n - a_n^+ a_c^+ a_c a_n$$

$$+ 2a_a^+ a_n^+ a_n a_a - 2a_a^+ a_{\bar{a}}^+ a_{\bar{n}} a_n|0\rangle)\delta_{ad}$$

$$+ 2(an|cn)(\langle 0|a_n^+ a_{\bar{n}}^+ a_{\bar{a}} a_a + a_n^+ a_{\bar{n}}^+ a_{\bar{c}} a_c - a_n^+ a_a^+ a_a a_n - a_n^+ a_c^+ a_c a_n$$

$$+ 2a_b^+ a_n^+ a_n a_b - 2a_b^+ a_{\bar{b}}^+ a_{\bar{n}} a_n|0\rangle)\delta_{bd}$$

$$+ 4(ac|nn)(\langle 0|a_n^+ a_a^+ a_a a_n + a_n^+ a_c^+ a_c a_n - 2a_n^+ a_b^+ a_b a_n|0\rangle)\delta_{bd}$$

$$+ 4(ad|nn)(\langle 0|a_n^+ a_a^+ a_a a_n + a_n^+ a_d^+ a_d a_n - 2a_n^+ a_b^+ a_b a_n|0\rangle)\delta_{bc}$$

$$+ 4(bc|nn)(\langle 0|a_n^+ a_b^+ a_b a_n + a_n^+ a_c^+ a_c a_n - 2a_n^+ a_a^+ a_a a_n|0\rangle)\delta_{ad}$$

$$+ 4(bd|nn)(\langle 0|a_n^+ a_b^+ a_b a_n + a_n^+ a_d^+ a_d a_n - 2a_n^+ a_a^+ a_a a_n|0\rangle)\delta_{ac} \Big\}$$

The Propagator matrix element P_{abcd} in the GTDA may be expressed using the following notation. Let

$$f_1 = (g_b g_d + g_a g_c) \quad ; \quad f_2 = (g_b g_c + g_a g_d)$$

we have,

$$1)\ P^{(s)}_{abcd} = 4(ab|cd)((f_1 + f_2)\langle 0|a^+_b a^+_d a_d a_b + a^+_a a^+_c a_c a_a - a^+_b a^+_c a_c a_b$$

$$- a^+_a a^+_d a_d a_a|0\rangle)$$

$$+ 2(ac|bd)(f_1\langle 0|a^+_b a^+_c a_c a_b - a^+_b a^+_d a_d a_b - a^+_a a^+_c a_c a_a + a^+_a a^+_d a_d a_a$$

$$+ a^+_a a^+_{\bar a} a_{\bar c} a_c + a^+_b a^+_{\bar b} a_{\bar d} a_d|0\rangle - f_2\langle 0|a^+_a a^+_{\bar a} a_{\bar d} a_d + a^+_b a^+_{\bar b} a_{\bar c} a_c|0\rangle)$$

$$+ 2(ad|bc)(f_2\langle 0|a^+_b a^+_c a_c a_b - a^+_b a^+_d a_d a_b - a^+_a a^+_c a_c a_a + a^+_a a^+_d a_d a_a$$

$$+ a^+_a a^+_{\bar a} a_{\bar d} a_d + a^+_b a^+_{\bar b} a_{\bar c} a_c|0\rangle - f_1\langle 0|a^+_a a^+_{\bar a} a_{\bar c} a_c + a^+_b a^+_{\bar b} a_{\bar d} a_d|0\rangle)$$

$$- \sum_n \Big\{((nb|nd)(f_1\langle 0|a^+_b a^+_{\bar b} a_{\bar n} a_n - a^+_b a^+_n a_n a_b + a^+_a a^+_n a_n a_a|0\rangle$$

$$- f_2\langle 0|a^+_a a^+_{\bar a} a_{\bar n} a_n|0\rangle) + 2(bd|nn)f_1\langle 0|a^+_b a^+_n a_n a_b - a^+_a a^+_c a_n a_a|0\rangle)\delta_{ac}$$

$$- ((an|nd)(f_2\langle 0|a^+_a a^+_{\bar a} a_{\bar n} a_n - a^+_a a^+_n a_n a_a + a^+_n a^+_b a_b a_n|0\rangle$$

$$- f_1\langle 0|a^+_b a^+_{\bar b} a_{\bar n} a_n|0\rangle) + 2(ad|nn)f_2\langle 0|a^+_a a^+_n a_n a_a - a^+_n a^+_b a_b a_n|0\rangle)\delta_{bc}$$

$$- ((nb|cn)(f_2\langle 0|a^+_b a^+_{\bar b} a_{\bar n} a_n - a^+_b a^+_n a_n a_b + a^+_a a^+_n a_n a_a|0\rangle$$

$$- f_1\langle 0|a_a^+ a_{\bar a}^+ a_{\bar n} a_n|0\rangle) + 2(bc|nn) f_2\langle 0|a_b^+ a_n^+ a_n a_b - a_a^+ a_n^+ a_n a_a|0\rangle)\delta_{ad}$$

$$- ((an|cn)(f_1\langle 0|a_a^+ a_{\bar a}^+ a_{\bar n} a_n - a_a^+ a_n^+ a_n a_a + a_n^+ a_b^+ a_b a_n|0\rangle$$

$$- f_2\langle 0|a_b^+ a_{\bar b}^+ a_{\bar n} a_n|0\rangle) + 2(ac|nn) f_1\langle 0|a_a^+ a_n^+ a_n a_a - a_n^+ a_b^+ a_b a_n|0\rangle)\delta_{bd}\Big\}$$

2) $F_{abcd}^{(t)} =$

$$2(ac|bd)(f_1\langle 0|a_b^+ a_c^+ a_c a_b - a_b^+ a_d^+ a_d a_b - a_a^+ a_c^+ a_c a_a + a_a^+ a_d^+ a_d a_a$$

$$+ a_a^+ a_{\bar a}^+ a_{\bar c} a_c + a_b^+ a_{\bar b}^+ a_{\bar d} a_d|0\rangle - f_2\langle 0|a_a^+ a_{\bar a}^+ a_{\bar d} a_d + a_b^+ a_{\bar b}^+ a_{\bar c} a_c|0\rangle)$$

$$+ 2(ad|bc)(f_2\langle 0|a_b^+ a_c^+ a_c a_b - a_b^+ a_d^+ a_d a_b - a_a^+ a_c^+ a_c a_a + a_a^+ a_d^+ a_d a_a$$

$$+ a_a^+ a_{\bar a}^+ a_{\bar d} a_d + a_b^+ a_{\bar b}^+ a_{\bar c} a_c|0\rangle - f_1\langle 0|a_a^+ a_{\bar a}^+ a_{\bar c} a_c + a_b^+ a_{\bar b}^+ a_{\bar d} a_d|0\rangle)$$

$$- \sum_n \Big\{((nb|nd)(f_1\langle 0|a_b^+ a_{\bar b}^+ a_{\bar n} a_n - a_b^+ a_n^+ a_n a_b + a_a^+ a_n^+ a_n a_a|0\rangle$$

$$- f_2\langle 0|a_a^+ a_{\bar a}^+ a_{\bar n} a_n|0\rangle) + 2(bd|nn) f_1\langle 0|a_b^+ a_n^+ a_n a_b - a_a^+ a_n^+ a_n a_a|0\rangle)\delta_{ac}$$

$$- ((an|nd)(f_2\langle 0|a_a^+ a_{\bar a}^+ a_{\bar n} a_n - a_a^+ a_n^+ a_n a_a + a_n^+ a_b^+ a_b a_n|0\rangle$$

$$- f_1\langle 0|a_b^+ a_{\bar b}^+ a_{\bar n} a_n|0\rangle) + 2(ad|nn) f_2\langle 0|a_a^+ a_n^+ a_n a_a - a_n^+ a_b^+ a_b a_n|0\rangle)\delta_{bc}$$

$$- ((nb|cn)(f_2\langle 0|a_b^+ a_{\bar b}^+ a_{\bar n} a_n - a_b^+ a_n^+ a_n a_b + a_a^+ a_n^+ a_n a_a|0\rangle$$

$$- f_1\langle 0|a_a^+ a_{\bar a}^+ a_{\bar n} a_n|0\rangle) + 2(bc|nn) f_2\langle 0|a_b^+ a_n^+ a_n a_b - a_a^+ a_n^+ a_n a_a|0\rangle)\delta_{ad}$$

$$+ ((an|cn)(f_1\langle 0|a_a^+ a_{\bar a}^+ a_{\bar n} a_n - a_a^+ a_n^+ a_n a_a + a_n^+ a_b^+ a_b a_n|0\rangle$$

$$- f_2\langle 0|a_b^+ a_{\bar b}^+ a_{\bar n} a_n|0\rangle) + 2(ac|nn) f_1\langle 0|a_a^+ a_n^+ a_n a_a - a_n^+ a_b^+ a_b a_n|0\rangle)\delta_{bd}\Big\}$$

APPENDIX 2
OPEN SHELL RPA MATRIX ELEMENTS

The types of matrix elements that are required to be evaluated may be split into two sections, i.e.

'A' block

a1) $\langle 0|[(g_b a^+_o a^+_{\bar{b}} a_a a_{\bar{o}} + g_a a^+_o a^+_{\bar{a}} a_b a_{\bar{a}} \; [K_H \; , \; g_d a^+_{\bar{o}} a^+_d a_{\bar{c}} a_a$

$\quad + g_c a^+_{\bar{o}} a^+_d a_{\bar{c}} a_o \;]]|0\rangle$

a2) $\langle 0|[(g_b \left(a^+_b a_a - a^+_{\bar{b}} a_{\bar{a}}\right) + g_a \left(a^+_a a_b - a^+_{\bar{a}} a_{\bar{b}}\right)[K_H, \; g_d \left(a^+_o a_d - a^+_{\bar{c}} a_{\bar{d}}\right)$

$\quad + g_c \left(a^+_d a_c - a^+_{\bar{d}} a_{\bar{c}}\right)]]|0\rangle$

a3) $\langle 0|[(g_b a^+_o a^+_{\bar{a}} a_a a_{\bar{o}} + g_a a^+_a a^+_{\bar{a}} a_b a_{\bar{o}} \; [K_H \; , \; g_d \left(a^+_c a_d - a^+_{\bar{c}} a_{\bar{d}}\right)$

$\quad + g_c \left(a^+_d a_c - a^+_{\bar{d}} a_{\bar{c}}\right)]]|0\rangle$

a4) $\langle 0|[(g_b \left(a^+_b a_a - a^+_{\bar{b}} a_{\bar{a}}\right) + g_a \left(a^+_a a_b - a^+_{\bar{a}} a_{\bar{b}}\right)[K_H \; , \; g_d a^+_{\bar{o}} a^+_d a_{\bar{c}} a_o$

$\quad + g_c a^+_{\bar{o}} a^+_d a_{\bar{c}} a_o \;]]|0\rangle$

a5) $\langle 0|[(g_b a^+_o a^+_{\bar{b}} a_a a_{\bar{o}} + g_a a^+_o a^+_{\bar{a}} a_b a_{\bar{o}} \; [K_H \; , \; g_d \left(a^+_c a_d + a^+_{\bar{c}} a_{\bar{d}}\right)$

$\quad - g_c \left(a^+_d a_c + a^+_{\bar{d}} a_{\bar{c}}\right)]]|0\rangle$

'B' block

b1) $\langle 0|[(g_b a^+_{\bar{o}} a^+_a a_{\bar{b}} a_o + g_a a^+_{\bar{c}} a^+_b a_{\bar{a}} a_a \; (K_H \; , \; g_d a^+_{\bar{a}} a^+_d a_{\bar{c}} a_o$

$\quad + g_c a^+_{\bar{o}} a^+_d a_{\bar{c}} a_o \;]]|0\rangle$

b2) $\langle 0|[(g_b \left(a^+_a a_b - a^+_{\bar{a}} a_{\bar{b}}\right) + g_a \left(a^+_b a_a - a^+_{\bar{b}} a_{\bar{a}}\right)[K_H, \; g_d \left(a^+_c a_d - a^+_{\bar{c}} a_{\bar{d}}\right)$

$\quad + g_c \left(a^+_d a_o - a^+_{\bar{d}} a_{\bar{c}}\right)]]|0\rangle$

$$b3)\ \langle 0|[g_b a^+_{\bar{o}} a^+_a a_{\bar{b}} a_o + g_a a^+_{\bar{o}} a^+_b a_{\bar{a}} a_o\ [K_H\ ,\ g_d\left(a^+_c a_d - a^+_{\bar{c}} a_{\bar{d}}\right)$$
$$+\ g_c\left(a^+_d a_c - a^+_{\bar{d}} a_{\bar{c}}\right)]]|o\rangle$$

$$b4)\ \langle 0|[g_b\left(a^+_a a_b - a^+_{\bar{a}} a_{\bar{b}}\right) + g_a\left(a^+_b a_a - a^+_{\bar{b}} a_{\bar{a}}\right)[K_H\ ,\ g_d a^+_{\bar{o}} a^+_d a_{\bar{c}} a_o$$
$$+\ g_c a^+_{\bar{o}} a^+_d a_{\bar{c}} a_o\ ]]|o\rangle$$

$$b5)\ \langle 0|[g_b a^+_{\bar{o}} a^+_a a_{\bar{b}} a_o + g_a a^+_{\bar{a}} a^+_b a_{\bar{a}} a_a\ [K_H\ ,\ g_d\left(a^+_c a_d + a^+_{\bar{c}} a_{\bar{d}}\right)$$
$$-\ g_c\left(a^+_d a_c + a^+_{\bar{d}} a_{\bar{c}}\right)]]|o\rangle$$

The expression for each term is as follows

Term a1) =

$$(ac|bd)\Big(g_b g_d\ \langle 0|a^+_o a^+_{\bar{b}} a^+_c a^+_{\bar{c}} a_{\bar{a}} a_a a_{\bar{b}} a_o\ +\ a^+_o a^+_{\bar{b}} a^+_c a^+_a a_a a_c a_{\bar{b}} a_o$$
$$-\ a^+_o a^+_{\bar{b}} a^+_b a^+_a a_a a_d a_{\bar{d}} a_o\ +\ a^+_o a^+_{\bar{b}} a^+_d a^+_a a_a a_d a_{\bar{b}} a_o$$
$$-\ a^+_o a^+_{\bar{b}} a^+_c a_c a_{\bar{b}} a_o|o\rangle$$

$$g_a g_c(\langle 0|a^+_o a^+_{\bar{a}} a^+_d a^+_{\bar{d}} a_{\bar{b}} a_b a_{\bar{a}} a_o\ +\ a^+_o a^+_{\bar{a}} a^+_d a^+_b a_b a_d a_{\bar{a}} a_o$$
$$-\ a^+_o a^+_{\bar{a}} a^+_a a^+_b a_b a_c a_{\bar{c}} a_o\ +\ a^+_o a^+_{\bar{a}} a^+_{\bar{c}} a^+_b a_b a_{\bar{c}} a_{\bar{a}} a_o$$
$$-\ a^+_o a^+_{\bar{a}} a^+_d a_d a_{\bar{a}} a_o|o\rangle)$$

$$-\ g_a g_d(\langle 0|a^+_o a^+_{\bar{a}} a^+_c a^+_{\bar{c}} a_{\bar{b}} a_b a_{\bar{a}} a_o\ -\ a^+_o a^+_{\bar{a}} a^+_a a^+_b a_b a_d a_{\bar{d}} a_o|0\rangle)$$

$$-\ g_b g_c(\langle 0|a^+_o a^+_{\bar{b}} a^+_d a^+_{\bar{d}} a_{\bar{a}} a_a a_{\bar{b}} a_o\ -\ a^+_o a^+_{\bar{b}} a^+_b a^+_a a_a a_c a_{\bar{c}} a_o|0\rangle)\Big)$$

$$+\ (ad|bc)\Big((g_b g_d - g_a g_c)(\langle 0|a^+_o a^+_{\bar{b}} a^+_c a^+_{\bar{c}} a_{\bar{a}} a_a a_{\bar{b}} a_o$$
$$+\ a^+_o a^+_{\bar{b}} a^+_b a^+_a a_a a_d a_{\bar{d}} a_o|0\rangle$$

$$+ g_a g_d(\langle 0|a_0^+ a_{\bar a}^+ a_c^+ a_c a_{\bar a} a_0|0\rangle + g_b g_c(\langle 0|a_0^+ a_{\bar b}^+ a_d^+ a_d a_{\bar b} a_0|0\rangle$$

$$+ (g_a g_d - g_b g_c)(\langle 0|a_0^+ a_{\bar a}^+ a_c^+ a_{\bar c}^+ a_{\bar b} a_b a_{\bar a} a_0 + a_0^+ a_{\bar a}^+ a_c^+ a_b^+ a_b a_c a_{\bar a} a_0$$

$$+ a_0^+ a_{\bar a}^+ a_b^+ a_{\bar d}^+ a_{\bar d} a_b a_{\bar a} a_0 - a_0^+ a_{\bar a}^+ a_a^+ a_b^+ a_b a_d a_{\bar d} a_0|0\rangle)\Big]$$

$$+ (aa|co)\Big(g_b g_d\langle 0|a_0^+ a_{\bar b}^+ a_c^+ a_0 a_{\bar b} a_0|0\rangle$$

$$+ (g_b g_d - g_a g_c)(\langle 0|a_0^+ a_{\bar b}^+ a_a^+ a_c^+ a_c a_a a_{\bar b} a_0 + a_0^+ a_{\bar b}^+ a_{\bar c}^+ a_c^+ a_a a_{\bar a} a_{\bar b} a_0|0\rangle)\delta_{\bar b\bar d}$$

$$+ (bo|do)\Big(g_a g_c\langle 0|a_0^+ a_{\bar a}^+ a_c^+ a_c a_{\bar a} a_0|0\rangle$$

$$+ (g_a g_c - g_b g_d)(\langle 0|a_0^+ a_{\bar b}^+ a_a^+ a_{\bar d}^+ a_{\bar d} a_a a_{\bar b} a_0 + a_0^+ a_{\bar b}^+ a_b^+ a_a^+ a_a a_d a_{\bar d} a_0|0\rangle)\delta_{ac}$$

$$+ (ao|do)\Big(g_a g_d\langle 0|a_0^+ a_{\bar b}^+ a_d^+ a_d a_{\bar b} a_0|0\rangle$$

$$+ (g_a g_d - g_b g_c)(\langle 0|a_0^+ a_{\bar b}^+ a_a^+ a_d^+ a_d a_a a_{\bar b} a_0 + a_0^+ a_{\bar b}^+ a_{\bar d}^+ a_d^+ a_a a_{\bar a} a_{\bar b} a_0|0\rangle)\delta_{bc}$$

$$+ (bo|co)\Big(g_b g_c\langle 0|a_0^+ a_{\bar a}^+ a_c^+ a_c a_{\bar a} a_0|0\rangle$$

$$+ (g_b g_c - g_a g_d)(\langle 0|a_0^+ a_{\bar a}^+ a_b^+ a_c^+ a_c a_b a_{\bar a} a_0 + a_0^+ a_{\bar a}^+ a_{\bar c}^+ a_c^+ a_b a_{\bar a} a_{\bar a} a_0|0\rangle)\delta_{ad}$$

$$+ \sum_{n\neq 0}(an|cn)\Big(- g_b g_d\langle 0|a_0^+ a_{\bar b}^+ a_n^+ a_n a_{\bar b} a_0|0\rangle + g_a g_c\langle 0|a_0^+ a_{\bar a}^+ a_n^+ a_n a_{\bar a} a_0|0\rangle$$

$$+ (g_b g_d - g_a g_c)(\langle 0|a_0^+ a_{\bar b}^+ a_a^+ a_n^+ a_n a_a a_{\bar b} a_0 - a_0^+ a_{\bar b}^+ a_{\bar n}^+ a_n^+ a_a a_{\bar a} a_{\bar b} a_0|0\rangle)\delta_{bd}\Big)$$

$$+ \sum_{n\neq 0}(bn|dn)\Big(- g_a g_c\langle 0|a_0^+ a_{\bar a}^+ a_n^+ a_n a_{\bar a} a_0|0\rangle + g_b g_d\langle 0|a_0^+ a_{\bar b}^+ a_n^+ a_n a_{\bar b} a_0|0\rangle$$

$$+ (g_a g_c - g_b g_d)(\langle 0|a_0^+ a_{\bar b}^+ a_a^+ a_n^+ a_n a_a a_{\bar b} a_0 - a_0^+ a_{\bar b}^+ a_b^+ a_a^+ a_a a_n a_{\bar n} a_0|0\rangle)\delta_{ac}\Big)$$

$$+ \sum_{n\neq 0}(an|dn)\Big(- g_b g_c\langle 0|a_0^+ a_{\bar b}^+ a_n^+ a_n a_{\bar b} a_0|0\rangle + g_a g_d\langle 0|a_0^+ a_{\bar a}^+ a_n^+ a_n a_{\bar a} a_0|0\rangle$$

$$+(g_b g_c - g_a g_d)(\langle 0|a_0^+ a_{\bar b}^+ a_a^+ a_n^+ a_n a_a a_{\bar b} a_0 - a_0^+ a_{\bar b}^+ a_{\bar n}^+ a_n^+ a_a a_{\bar a} a_{\bar b} a_0|0\rangle)\delta_{bc}\Big)$$

$$+\sum_{n\neq 0}(bo|cn)\Big(-g_a g_d\langle 0|a_0^+ a_{\bar a}^+ a_n^+ a_n a_{\bar a} a_0|0\rangle + g_b g_c\langle 0|a_0^+ a_{\bar b}^+ a_n^+ a_n a_{\bar b} a_0|0\rangle$$
$$+(g_a g_d - g_b g_c)(\langle 0|a_0^+ a_{\bar b}^+ a_a^+ a_n^+ a_n a_a a_{\bar b} a_0 + a_0^+ a_{\bar b}^+ a_b^+ a_a^+ a_a a_n a_{\bar n} a_0|0\rangle)\delta_{ad}\Big)$$

$$+(ac|oo)\Big(g_b g_d\langle 0|a_0^+ a_{\bar b}^+ a_{\bar b} a_0|0\rangle - g_a g_c\langle 0|a_0^+ a_{\bar a}^+ a_{\bar a} a_0|0\rangle$$
$$-(g_b g_d - g_a g_c)\langle 0|a_0^+ a_{\bar b}^+ a_a^+ a_a a_{\bar b} a_0|0\rangle\Big)\delta_{bd}$$

$$+(bd|oo)\Big(-g_b g_d\langle 0|a_0^+ a_{\bar b}^+ a_{\bar b} a_0|0\rangle + g_a g_c\langle 0|a_0^+ a_{\bar a}^+ a_{\bar a} a_0|0\rangle$$
$$+(g_b g_d - g_a g_c)\langle 0|a_0^+ a_{\bar b}^+ a_a^+ a_a a_{\bar b} a_0|0\rangle\Big)\delta_{ac}$$

$$+(ad|oo)\Big(g_b g_c\langle 0|a_0^+ a_{\bar b}^+ a_{\bar b} a_0|0\rangle - g_a g_d\langle 0|a_0^+ a_{\bar a}^+ a_{\bar a} a_0|0\rangle$$
$$-(g_b g_c - g_a g_d)\langle 0|a_0^+ a_{\bar b}^+ a_a^+ a_a a_{\bar b} a_0|0\rangle\Big)\delta_{bc}$$

$$+(bc|oo)\Big(-g_b g_d\langle 0|a_0^+ a_{\bar b}^+ a_{\bar b} a_0|0\rangle + g_a g_c\langle 0|a_0^+ a_{\bar a}^+ a_{\bar a} a_0|0\rangle$$
$$-(g_b g_d - g_a g_c)\langle 0|a_0^+ a_{\bar b}^+ a_a^+ a_a a_{\bar b} a_0|0\rangle\Big)\delta_{ad}$$

$$+2\sum_{n\neq 0}(ac|nn)\Big(g_b g_d\langle 0|a_0^+ a_{\bar b}^+ a_n^+ a_n a_{\bar b} a_0|0\rangle - g_a g_c\langle 0|a_0^+ a_{\bar a}^+ a_n^+ a_n a_{\bar a} a_0|0\rangle$$
$$-(g_b g_d - g_a g_c)(\langle 0|a_0^+ a_{\bar b}^+ a_a^+ a_n^+ a_n a_a a_{\bar b} a_0|0\rangle)\delta_{bd}\Big)$$

$$+2\sum_{n\neq 0}(bd|nn)\Big(-g_b g_d\langle 0|a_0^+ a_{\bar b}^+ a_n^+ a_n a_{\bar b} a_0|0\rangle + g_a g_c\langle 0|a_0^+ a_{\bar a}^+ a_n^+ a_n a_{\bar a} a_0|0\rangle$$
$$+(g_b g_d - g_a g_c)(\langle 0|a_0^+ a_{\bar b}^+ a_a^+ a_n^+ a_n a_a a_{\bar b} a_0|0\rangle)\delta_{ac}\Big)$$

$$+2\sum_{n\neq 0}(ad|nn)\Big(g_b g_c\langle 0|a_0^+ a_{\bar b}^+ a_n^+ a_n a_{\bar b} a_0|0\rangle + g_a g_d\langle 0|a_0^+ a_{\bar a}^+ a_n^+ a_n a_{\bar a} a_0|0\rangle$$

$$-(g_b g_c - g_a g_d)(\langle 0|a_o^+ a_{\bar{b}}^+ a_a^+ a_n^+ a_n a_a a_{\bar{b}} a_o|0\rangle)\delta_{bc}\Big)$$

$$+2\sum_{n\neq o}(bc|nn)\Big(- g_b g_c \langle 0|a_o^+ a_{\bar{n}}^+ a_n^+ a_n a_{\bar{b}} a_o|0\rangle + g_a g_d \langle 0|a_o^+ a_{\bar{a}}^+ a_n^+ a_n a_{\bar{a}} a_o|0\rangle$$

$$+(g_b g_c - g_a g_d)(\langle 0|a_o^+ a_{\bar{b}}^+ a_a^+ a_n^+ a_n a_a a_{\bar{b}} a_o|0\rangle)\delta_{ad}\Big)$$

Term a2) is identical to the expression obtained for the closed shell GAGF triplet ($m_a=0$) propagator.

Term a3) =

$$(aa|co)\Big(g_b g_d \langle 0|a_o^+ a_{\bar{b}}^+ a_{\bar{b}} a_o|0\rangle + g_a g_c \langle 0|a_o^+ a_{\bar{a}}^+ a_{\bar{a}} a_o|0\rangle$$

$$- g_b g_d \langle 0|a_o^+ a_{\bar{b}}^+ a_a^+ a_a a_{\bar{b}} a_o|0\rangle + g_a g_c \langle 0|a_o^+ a_{\bar{a}}^+ a_b^+ a_b a_{\bar{a}} a_o|0\rangle\Big)\delta_{bd}$$

$$+ (bo|do)\Big(g_b g_d \langle 0|a_o^+ a_{\bar{b}}^+ a_{\bar{b}} a_o|0\rangle + g_a g_c \langle 0|a_o^+ a_{\bar{a}}^+ a_{\bar{a}} a_o|0\rangle$$

$$- g_b g_d \langle 0|a_o^+ a_{\bar{b}}^+ a_a^+ a_a a_{\bar{b}} a_o|0\rangle + g_a g_c \langle 0|a_o^+ a_{\bar{a}}^+ a_b^+ a_b a_{\bar{a}} a_o|0\rangle\Big)\delta_{ac}$$

$$+ (aa|do)\Big(g_b g_c \langle 0|a_o^+ a_{\bar{b}}^+ a_{\bar{b}} a_o|0\rangle\delta_{\bar{b}\bar{d}} + g_a g_d \langle 0|a_o^+ a_{\bar{a}}^+ a_{\bar{a}} a_o|0\rangle\delta_{bc}$$

$$- g_b g_c \langle 0|a_o^+ a_{\bar{b}}^+ a_a^+ a_a a_{\bar{b}} a_o|0\rangle\delta_{\bar{b}\bar{d}} + g_a g_d \langle 0|a_o^+ a_{\bar{a}}^+ a_b^+ a_b a_{\bar{a}} a_o|0\rangle\delta_{bc}\Big)$$

$$+ (bo|ca)\Big(g_b g_c \langle 0|a_o^+ a_{\bar{b}}^+ a_{\bar{b}} a_o|0\rangle\delta_{ac} + g_a g_d \langle 0|a_o^+ a_{\bar{a}}^+ a_{\bar{a}} a_o|0\rangle\delta_{\bar{a}\bar{d}}$$

$$- g_b g_c \langle 0|a_o^+ a_{\bar{b}}^+ a_a^+ a_a a_{\bar{b}} a_o|0\rangle\delta_{ac} + g_a g_c \langle 0|a_o^+ a_{\bar{a}}^+ a_b^+ a_b a_{\bar{a}} a_o|0\rangle\delta_{\bar{a}\bar{d}}\Big)$$

Term a4) =

$$(ao|ca)\Big[g_bg_d(\langle 0|a_o^+a_b^+a_ba_o - a_a^+a_a^+a_aa_o|0\rangle$$
$$+(g_bg_d + g_ag_c)\langle 0|a_o^+a_a^+a_c^+a_ca_aa_a - a_o^+a_b^+a_c^+a_ca_ba_a|0\rangle\Big)\delta_{bd}$$

$$+ (bo|da)\Big[g_ag_c(\langle 0|a_a^+a_a^+a_aa_o - a_o^+a_b^+a_ba_a|0\rangle$$
$$+(g_bg_d + g_ag_c)\langle 0|a_a^+a_b^+a_d^+a_da_ba_o - a_o^+a_a^+a_d^+a_da_aa_o|0\rangle\Big)\delta_{ac}$$

$$+ (ao|do)\Big\{g_bg_c(\langle 0|a_o^+a_b^+a_ba_o - a_o^+a_a^+a_aa_o|0\rangle$$
$$+(g_bg_c + g_ag_d)\langle 0|a_o^+a_a^+a_d^+a_da_aa_o - a_o^+a_b^+a_d^+a_da_ba_a|0\rangle\Big)\delta_{bc}$$

$$+ (bo|ca)\Big[g_ag_d(\langle 0|a_o^+a_a^+a_aa_o - a_o^+a_b^+a_ba_a|0\rangle$$
$$+(g_bg_c + g_ag_d)\langle 0|a_o^+a_b^+a_c^+a_ca_ba_o - a_o^+a_a^+a_c^+a_ca_aa_o|0\rangle\Big)\delta_{ad}$$

Term a5) =

$$(ao|co)\Big(-g_ag_c\langle 0|a_o^+a_{\bar{a}}^+a_{\bar{a}}a_o|0\rangle - g_bg_d\langle 0|a_o^+a_{\bar{b}}^+a_{\bar{b}}a_a|0\rangle$$
$$+ (g_ag_c - g_bg_d)\langle 0|a_o^+a_a^+a_b^+a_ba_aa_o|0\rangle\Big)\delta_{bd}$$

$$+ (ao|do)\Big(g_ag_d\langle 0|a_o^+a_{\bar{a}}^+a_{\bar{a}}a_o|0\rangle + g_bg_c\langle 0|a_o^+a_{\bar{b}}^+a_{\bar{b}}a_o|0\rangle$$
$$+ (g_bg_c - g_ag_d)\langle 0|a_o^+a_a^+a_b^+a_ba_aa_a|0\rangle\Big)\delta_{bc}$$

$$+ (bo|co)\Big(-g_ag_d\langle 0|a_o^+a_{\bar{a}}^+a_{\bar{a}}a_a|0\rangle - g_bg_c\langle 0|a_o^+a_{\bar{b}}^+a_{\bar{b}}a_o|0\rangle$$
$$+ (g_bg_c - g_ag_d)\langle 0|a_o^+a_a^+a_b^+a_ba_aa_o|0\rangle\Big)\delta_{ad}$$

$$+ (bo|do)\Big(g_ag_c\langle 0|a_o^+a_{\bar{a}}^+a_{\bar{a}}a_o|0\rangle + g_bg_d\langle 0|a_o^+a_{\bar{b}}^+a_{\bar{b}}a_o|0\rangle$$

$$+ (g_a g_c - g_b g_d)\langle 0|a^+_o a^+_a a^+_b a_b a_a a_o|0\rangle\Big)\delta_{ac}$$

The following are the contributions to the B block,

Term b1) = 0

Term b2) is same as the closed shell triplet (m_s = 0) RPA

Term b3) =

$$(bo|do)(g_a g_d\langle 0|a^+_a a^+_{\bar a} a_{\bar a} a_a - a^+_a a^+_b a_b a_a + a^+_d a^+_{\bar d} a_{\bar d} a_d - a^+_a a^+_d a_d a_c|0\rangle$$

$$+ g_b g_c\langle 0|a^+_b a^+_{\bar b} a_{\bar b} a_b - a^+_a a^+_b a_b a_a + a^+_c a^+_{\bar c} a_{\bar c} a_c - a^+_c a^+_d a_d a_c|0\rangle)\delta_{ac}$$

$$+ (bo|co)(g_a g_c\langle 0|a^+_a a^+_{\bar a} a_{\bar a} a_a - a^+_a a^+_b a_b a_a + a^+_c a^+_{\bar c} a_{\bar c} a_c - a^+_c a^+_d a_d a_c|0\rangle$$

$$+ g_b g_d\langle 0|a^+_b a^+_{\bar b} a_{\bar b} a_b - a^+_a a^+_b a_b a_a + a^+_d a^+_{\bar d} a_{\bar d} a_d - a^+_c a^+_d a_d a_c|0\rangle)\delta_{ad}$$

$$+ (ao|do)(g_b g_d\langle 0|a^+_b a^+_{\bar b} a_{\bar b} a_b - a^+_a a^+_b a_b a_a + a^+_d a^+_{\bar d} a_{\bar d} a_d - a^+_c a^+_d a_d a_c|0\rangle$$

$$+ g_a g_c\langle 0|a^+_a a^+_{\bar a} a_{\bar a} a_a - a^+_a a^+_b a_b a_a + a^+_c a^+_{\bar c} a_{\bar c} a_c - a^+_c a^+_d a_d a_c|0\rangle)\delta_{bc}$$

$$+ (ao|co)(g_a g_d\langle 0|a^+_a a^+_{\bar a} a_{\bar a} a_a - a^+_a a^+_b a_b a_a + a^+_d a^+_{\bar d} a_{\bar d} a_d - a^+_c a^+_d a_d a_c|0\rangle$$

$$+ g_b g_c\langle 0|a^+_b a^+_{\bar b} a_{\bar b} a_b - a^+_a a^+_b a_b a_a + a^+_c a^+_{\bar c} a_{\bar c} a_c - a^+_c a^+_d a_d a_c|0\rangle)\delta_{bd}$$

Term b4) =

$$(ao|co)\Big(g_a g_d(\langle 0|a^+_o a^+_b a_b a_o - a^+_o a^+_a a_a a_o|0\rangle$$

$$+(g_a g_d + g_b g_c)\langle 0|a_o^+ a_a^+ a_c^+ a_c a_a a_o - a_o^+ a_b^+ a_c^+ a_c a_b a_o|0\rangle\Big\}\delta_{bd}$$

$$+ (bo|do)\Big\{g_b g_c(\langle 0|a_o^+ a_a^+ a_a a_o - a_o^+ a_b^+ a_b a_o|0\rangle$$
$$+(g_a g_d + g_b g_c)\langle 0|a_o^+ a_b^+ a_d^+ a_d a_b a_o - a_o^+ a_a^+ a_d^+ a_d a_a a_o|0\rangle\Big\}\delta_{ac}$$

$$+ (ao|do)\Big\{g_a g_c(\langle 0|a_o^+ a_b^+ a_b a_o - a_o^+ a_a^+ a_a a_o|0\rangle$$
$$+(g_a g_c + g_b g_d)\langle 0|a_o^+ a_a^+ a_d^+ a_d a_a a_o - a_o^+ a_b^+ a_d^+ a_d a_b a_o|0\rangle\Big\}\delta_{bc}$$

$$+ (bo|co)\Big\{g_b g_d(\langle 0|a_o^+ a_a^+ a_a a_o - a_o^+ a_b^+ a_b a_o|0\rangle$$
$$+(g_a g_c + g_b g_d)\langle 0|a_o^+ a_b^+ a_c^+ a_c a_b a_o - a_o^+ a_a^+ a_c^+ a_c a_a a_o|0\rangle\Big\}\delta_{ad}$$

Term b5) =

$$(bo|do)(g_a g_d\langle 0|a_a^+ a_{\bar{a}}^+ a_{\bar{a}} a_a - a_a^+ a_b^+ a_b a_a|0\rangle$$
$$- g_b g_c\langle 0|a_b^+ a_{\bar{b}}^+ a_{\bar{b}} a_b - a_a^+ a_b^+ a_b a_a|0\rangle)\delta_{ac}$$
$$+ (bo|co)(-g_a g_c\langle 0|a_a^+ a_{\bar{a}}^+ a_{\bar{a}} a_a - a_a^+ a_b^+ a_b a_a|0\rangle$$
$$+ g_b g_d\langle 0|a_b^+ a_{\bar{b}}^+ a_{\bar{b}} a_b - a_a^+ a_b^+ a_b a_a|0\rangle)\delta_{ad}$$
$$+ (co|do)(g_b g_d\langle 0|a_b^+ a_{\bar{b}}^+ a_{\bar{b}} a_b - a_a^+ a_b^+ a_b a_a|0\rangle$$
$$- g_a g_c\langle 0|a_a^+ a_{\bar{a}}^+ a_{\bar{a}} a_a - a_a^+ a_b^+ a_b a_a|0\rangle)\delta_{bc}$$
$$+ (ao|co)(g_a g_d\langle 0|a_a^+ a_{\bar{a}}^+ a_{\bar{a}} a_a - a_a^+ a_b^+ a_b a_a|0\rangle$$
$$- g_b g_c\langle 0|a_b^+ a_{\bar{b}}^+ a_{\bar{b}} a_b - a_a^+ a_b^+ a_b a_a|0\rangle)\delta_{bd}$$

BIBLIOGRAPHY

1. J. Linderberg & N. Y. Ohrn, "Propagators in Quantum Chemistry" (Academic Press, London, 1973)

2. R. P. Feynman, Rev. Mod. Phys. 20, 367(1948); J. Schwinger, Proc. Nat. Acad. Sci. U.S. 37, 452(1951)

3. T. Matsubara, Prog. Theor. Phys. 23, 629(1955)

4. D. N. Zuberev, Soviet Physics Uspekhi, Vol. 3(5); 320(1960)

5. P. M. Dirac, Proc. Cambridge Phil. Soc. 26, 376[5.10] (1930)

6. D. Bohm and D. Pines, Phys. Rev. 92, 609(1953)

7. P. Ring and P. Schuck, "The Nuclear Many-Body Problem" (Springer-Verlag, New York, 1980)

8. D. J. Thouless, "The Quantum Mechanics Of Many-Body Systems" (Academic Press, New York, 1961)

9. E. Dalgaard; Int. Journal Quantum Chemistry, 15, 169(1979)

10. D. J. Rowe, Rev. Mod. Phys. 40, 153(1968); T. Shibuya and V. Mckoy, Phys. Rev. A 2, 2208(1970)

11. J. Linderberg and M. Ratner, Chem. Phys. Lett. 6, 37 (1970), J. Linderberg, P. Jørgensen, J. Oddershede, and M. Ratner, J. Chem. Phys. 56, 6213(1972), P. Jørgensen and J. Oddershede, J. Chem. Phys 57 277 (1972); P. Jørgensen, J. Oddershede and M. Ratner, J. Chem. Phys. 61 710(1974).

12. J. S. Rose, T. Shibuya and V. Mckoy, J. Chem. Phys. 58, 500(1973); T. N. Rescigno et al., Chem. Phys. Lett. 15, 307(1977).

13. J. Oddershede, Adv. in Quantum Chem. 11, 275(1978)

14. J. Linderberg and N. Y. Ohrn, Int. J. Quant. Chem. 12, 161(1977)

15. N. Y. Ohrn and J. Linderberg, Int. J. Quant. Chem. 15 343(1979)

16. J. Bardeen, L. N. Cooper and J. R. Schriffer, Phys. Rev. 108, 1175(1957).

17. J. M. Blatt, "Theory of Superconducting Systems" in Pure and applied physics 17, (Academic Press, New York, 1964)

18. H. Kurtz, N. Elander, O. Goscinski, and E. Sangfelt, Int. J. Quant. Chem. S15, 143(1991)

19. P. Swanstrøm and F. Jørgensen, J. Chem. Phys. 71(11), 4652(1979)

20. O. Goscinski and B. Lukman, Chem. Phys. Lett., 7, 573(1970)

21. B. Weiner and O. Goscinski, Int. J. Quant. Chem. 21, 369(1982)

22. J. Simons, J. Chem. Phys. 64, 4541(1976); B. Manne, Chem. Phys. Lett. 45, 470(1977)

23. P. O. Lowdin, Phys. Rev. A, 139, 357(1965)

24. P. O. Lowdin, Int. J. Quant. Chem. 4, 231(1971)

25. P. O. Lowdin, and P. Liedmer, Int. J. Quant. Chem. 28, 161(1969)

26. P. Jorgensen, Ann. Rev. Phys. Chem. 26, 1013(1975)

27. S. J. Aa. Jensen, B. Weiner, and N. Y. Ohrn, J. Chem. Phys. 90(5), 2009(1984)

28. P. Jorgensen and J.Simons, "Second Quantization Methods in Quantum Chemistry", (Academic Press, New York, 1981)

29. D. J. Thouless, Nucl. Phys. 22, 79(1961)

30. Private communication with Dr. B. Weiner

31. P. Jorgensen and J. Lindarberg, Int. J. Quant. Chem. 4, 587(1970)

32. S. Aa. J. Jensen, Ph.D Thesis, Aarhus, University; J. V. Ortiz, Ph.D Dissertation, University of Florida

33. B. Weiner and O.Goscinski, Int. J. Quant. Chem. 18, 1109(1980)

34. A. J. Coleman, J. Math. Phys. 13, 214(1972); ibid. 6, 1425(1965)

35. K. Nakamura, Prog. Theo. Phys.(Kyoto) 21, 713(1959)

36. E. Sangfelt, O. Goscinski, N. Elander, and H. Kurtz, Int. J. Quant. Chem. S15, 133(1991)

37. E. Sangfelt, O. Goscinski, J. Chem. Phys. 92(9), 4187(1985)

38. A. Igawa and H. Fukutome, Prog. Theor. Phys. 54, 1266(1975); E. Dalgaard and P. Jorgensen, J. Chem. Phys. 69, 3833(1978)

39. A. J. Coleman, Rev. Mod. Phys. 35, 668(1963); H. Kummer, J. Math. Phys. 8, 2063(1967); ibid. 11, 449(1970); A. J. Coleman, Int. J. Quant. Chem. 13, 67(1978)

40. B. Weiner and O. Goscinski, Phys. Rev. A, 22(6) 2374 (1980).

41. J. V. Ortiz, B. Weiner, and N. Y. Ohrn, Int. J. Quant. Chem., S15, 113(1981)

42. H. Aa. J. Jensen, B. Weiner, and Y. Ohrn, Int. J. Quant. Chem. S16, 615(1982)

43. B. Weiner, Int. J. Quant. Chem. 28, 61(1985)

44. E. Sangfelt, H. Kurtz, N. Elander and O. Goscinski, J. Chem. Phys. 81(9), 3976(1984)

45. F. L. Pilar, "Elementary Quantum Chemistry" (McGraw-Hill, New York, 1968)

46. R. Pauncz, "Spin Eigenfunctions" (Plenum Press, New York, 1979)

47. C. E. Moore, "Atomic Energy Levels" (Nat. Bur. Stand. Circ. US G.P.O. Washington D.C., 1949), Vol. 4, p. 967

48. T. H. Dunning and P. J. Hay, "Modern Theoretical Chemistry, Methods in Electronic Structure", Edited by H. Schaefer III (Plenum, New York, 1977), Vol. 3

49. B. Weiner, H. Kurtz and Y. Ohrn, "In Comparison Of Ab Initio Calculations With Experiment: State Of The Art", Edited by R. J. Bartlett (Reidel, Dordrecht, Netherlands, 1985) in press.

50. K. K. Docken and J. Hinze, J. Chem. Phys. 57, 4928(1972); ibid. 57, 4936(1972); H. Partridge and S. R. Langhoff, J. Chem. Phys. 74, 2361(1981)

51. K. R. Way and W. C. Stwalley, J. Chem. Phys. 59, 5298(9173)

52. H. E. White, "Introduction To Atomic Spectra" (McGraw-Hill, New York, 1934), p. 179

53. I. Martinson, A. Gaupp and L. J. Curtis, J. Phys. B 7, L463(1974).

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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